Study on Distribution and Behavior of PFOS (Perfluorooctane Sulfonate) and PFOA (Perfluorooctanoate) in Water Environment(Dissertation_全文)

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Study on Distribution and Behavior of PFOS (Perfluorooctane Sulfonate) and PFOA (Pefluorooctanoate) in Water Environment

（水環境における PFOS (ペルフルオロオクタンスルホン酸)
および PFOA（ペルフルオロオクタン酸）の分布と挙動に関する研究）

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ABSTRACT

PFOS (perfluoroctane sulfonate) and PFOA (perfloroctanoate) are man-made surfactants having wide range of industrial and commercial applications for decades. In the beginning of this decade, researcher found that they were ubiquitous in living organism and human, and that they possibly had characteristics of persistent organic pollutants. Therefore, there is an emerging need to study PFOS and PFOA contamination environment, particularly in the water environment.

The research aims at examination of spatial distribution and behavior of PFOS and PFOA in water environment of several countries, with focus on new places where examination has never been conducted. Therefore, the method to analyze PFOS and PFOA in environmental water was developed. Sampling surveys were conducted to collect various types of water including surface water, wastewater treatment plant (WWTP) discharges, and tap water from various locations for analysis of PFOS and PFOA. Distribution and behavior of PFOS and PFOA were examined as three main parts. Firstly, it was to examine spatial distribution of PFOS and PFOA concentrations in environmental water. Then, it was to investigate concentrations in tap waters and its relationship to environmental water concentrations. Finally, mass flux analysis was conducted to search for sources of contaminants in environmental water in highly contaminated areas.

A qualified method for analysis of PFOS and PFOA in environmental water was developed. Analysis was conducted by SPE (solid phase extraction) coupled with HPLC-MS (high performance liquid chromatography tandem mass spectrometry) quantification. The limit of quantifications (LOQs) were 0.05-0.1 ng/L PFOS and 0.1-0.2 ng/L PFOA with water concentration factor of 1000-2000 times. Standard curve for HPLC-MS were performed well with R^2 values above 0.99. Extraction recoveries were within 90%-110%.

Distribution of PFOS and PFOA concentration in surface water in various areas: Yodo River (N=34), Kinki (N=15) (Japan), Shenzhen (N=9) (China), Hanoi (N=12) (Vietnam), Phong River (N=29) and Chao Phraya River (N=15) (Thailand), Johor Barhu (N=6) and Kota Kinabalu (N=21) (Malaysia), Singapore (N=24), Orebro (N=12) (Sweden) and Turkey (N=5) were recognized. PFOS and PFOA water concentration levels in those areas,

except for Japan, have never been reported in the literatures. Several conclusions were obtained as follows. **1)** Overall 90% and 85% of sampling locations (*N*=185) had surface water concentration above LOQs for PFOS and PFOA respectively. Average concentrations at individual sampling locations varied from <0.05 ng/L to 67 ng/L for PFOS and < 0.1ng/L to 21,600 ng/L PFOA. Medians of PFOS concentration (ng/L) in individual areas are ranked as followes: Johor Barhu (7.1), Singapore (4.7), Yodo River (3.5), Shenzhen (2.5), Chao Phraya River (1.6), Kinki (1.5), Turkey (1.0), Orebro (0.9), Phong River (0.2), Kota Kinabalu (0.1), Hanoi (0.1). Those for PFOA were: Yodo River (34.4), Singapore (16.4), Shenzhen (14.3), Johor Bahru (12.9); Kinki (3.3); Chao Phraya River (4.2); Turkey (3.1); Hanoi (0.9); Phong River (0.7); Kota Kinabalu (0.2); Orebro (0.1). The results suggest ubiquitous pollution of PFOS and PFOA in environmental water at ng/L order of concentration. **2)** It is observed that high concentration levels often found for surface waters of urbanized and industrialized areas (Yodo River, Shenzhen, Johor Barhu, Singapore) while low concentration levels were found for surface water of the other areas which are non-populated or non-industrialized (Orebro, Phong River, Kota Kinabalu, Hanoi). However, relatively low concentration levels found in surveyed areas, in fact, were higher than reported values for oceanic water suggesting affect from human activity. **3)** Within an area, WWTP discharges often had concentrations higher than those of surface waters did. **4)** 85% of sampling locations had ratio of PFOS concentration to PFOA concentration (PFOS/PFOA ratio) within 0.01-1 indicating that PFOA concentration was typically higher than PFOS. The ratio often fluctuated in a narrow range indicating that PFOS and PFOA often co-exist. In Japan, PFOS/PFOA ratio fluctuated around 0.1 in Yodo River but went down to 0.001 in Ai River, where a PFOA concentration were repeatedly found at several μg/L indicating a separate point source of PFOA.

Concentration levels of PFOS and PFOA in drinking water in the Yodo River (*N*=15), in other locations in Japan (*N*=37) and outside Japan (*N*=30) were reported. The majority of samples had concentrations above LOQs for both PFOS and PFOA. Geomean (ranges) of PFOS concentration (ng/L) were 2.65 (0.9-8.4); 0.48 (0.01-9.13); and 0.50 (0.03-13.8) and those of PFOA were 11.8 (6.4-42.4); 1.4 (0.03-15.1), and 1.1 (0.05-109.3) for the three groups respectively. This indicates that the concentrations of PFOS and PFOA in Yodo River were approximately five to ten times higher than those in other groups. The differences were significant with $p<0.05$ for both PFOS and PFOA. It is notable that concentrations in the other groups were highly fluctuated (CV>1.5 typically), and concentrations in several areas such as Tokyo, Bangkok, Shenzhen were relatively high. Overall, it was found increasing trends of tap water concentrations versus surrounding surface water concentrations for both PFOS and PFOA. Case studies in Kinki region

(Japan) and Istanbul (Turkey) indicated similar concentrations of PFOS and PFOA in tap water to those in the water sources. It is suggested that PFOS and PFOA in environment water were not effectively removed through water treatment steps.

It was understood mass behavior and sources of PFOS and PFOA in Yodo River, Ai River (Japan) and Singapore, where relatively high levels of PFOS and PFOA concentrations were found. Firstly, mass flux was estimated indicating possible discharges of 15 kg/year PFOS and 120 kg/year PFOA from Yodo River to Osaka Bay and a possible discharge of several tons/year of PFOA from Ai River to Osaka Bay in Japan. In Singapore, it was estimated possible discharges of 55 kg/year PFOS and 39 kg/year of PFOA from WWTPs to Johor Strait and Singapore Strait. Secondly, it was found that sources of PFOS and PFOA in Yodo River was significantly contributed (70% for PFOS and 45% for PFOA) by several WWTP discharges located in Kyoto City and upstream basin of the Uji river, which totally had catchments area and population of approximately 5% and 30% of those in the whole basin respectively. In Ai River, estimated mass flux of tons/year of PFOA was mainly contributed by a WWTP discharge. Finally, among WWTP discharges, analysis of PFOS and PFOA mass flux in relation with population and domestic water quality items suggests there was little relation of PFOS and PFOA with domestic activities. In Singapore, total mass flux from all WWTP discharges was mainly contributed (80%) by two WWTP which receives a large amount of industrial wastewater.

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LIST OF ABBREVIATIONS

σ	: geometric standard deviation
BRG.	: Bridge
Cnl.	: Canal
CV	: coefficient of variation
D.	: Dam
GM	: geometric mean
HUT	: Hanoi University of Technology
ITU	: Istanbul Technical University
KKU	: Khon Kean University
LC_{50}	: Lethal dose: the amount of a material, given all at once, which causes the death of 50% (one half) of a group of test animals
LOAEL	: lowest-observed-adverse-effect-level
MU	: Mahidol University
N	: number of sampling locations (or samples)
NOAEL	: no-observed-adverse-effect-level
NOEC	: non-observed effect concentration
NUS	: National University of Singapore
OU	: Orebro University
PFCAs	: perfluorinated carboxylates
PFCs	: perflorinated compounds
PFOA	: perfuoroctanoate anion
PFOS acid	: perfluoroctanesulfonic acid
PFOS	: perfluoroctanesulfonate anion
POSF	: perfluorooctanesulfonyl fluoride
R.	: River
Res.	: Reservoir
TEFLON	: A trademark used for a waxy, opaque material, polytetrafluoroethylene, employed as a coating on cooking utensils and in industrial applications to prevent sticking
TUM	:Tsinghua University in Shenzhen
UMS	:University Malaysia Sabah
UTM	:University Technology Malaysia
WWTP(s)	: wastewater treatment plant(s)

CHAPTER I

INTRODUCTION

I.1 RESEARCH BACKGROUND

I.1.1 Problem of PFOS and PFOA is an emerging concern

PFOS (perfluorooctane sulfonate) and PFOA (perfluorooctanoate) are anions of artificial compounds that have surfactant property. These compounds, which have been produced since 1950s, are applied in various industrial sectors such as paper and textile industry and involved in various commercial products such as aqueous fire fighting foam, Teflon, and Gortex. PFOS and PFOA are intensively produced in the last decade but production of PFOS was stopped in 2002 by a major world producer in USA (3M Company). Reasons for the cease of production includes its ubiquitous appearance in various living organism including human blood (Kannan *et al.* 2001, 2004) and its potential toxicity to human (Gilliland and Mandel 1993, Alexander *et al.* 2004).

Because PFOS and PFOA are extremely persistent and potentially toxic, they are concerned in environmental field. PFOS is also bioaccumulative (Martin *et al.* 2003, Taniyasu *et al.* 2003) and recently are considered as a new kind of POPs (Persistent Organic Pollutants) (UNEP 2006). Environmental behavior and fate of PFOS and PFOA is not well understood thus, there is a large room for environmental researchers. There is an increasing trend of research on PFOS and PFOA as shown in **Figure 1.1**. Data were obtained according to key word searches in MEDLINE for C8, PFOS, PFOA, perfluorinated, and perfluoralkyl.

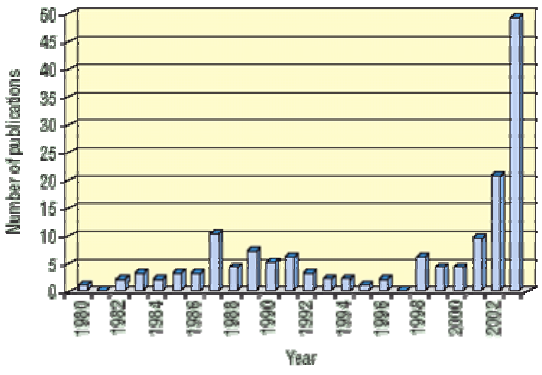


Figure 1.1 Number of research related to PFOS and PFOA (Martin *et al.* 2004)

I.1.2 PFOS and PFOA in surface water

Water is the most non-biota environmental compartment of concern for PFOS and PFOA because these

compounds have moderate water solubility, while atmospheric PFOS and PFOA might be not as such concern because of their involatile characteristic. Since PFOS and PFOA started to have emerging concerns in early this century, majority of research on these compounds has been focused on biota levels as well as toxicity. In comparison with data in biota, data of PFOS and PFOA in non-biota environmental were less.

Recognition concentration is the first step in order to control contaminant. Limited data in literature are not enough to understand the contamination a local scale in a large part of the world as well as not enough to understand behavior of PFOS and PFOA in a global scale. In terms of inland surface water, contamination was reported only in USA, Europe and Japan (**Figure 1.2**). There is a big room for investigation of the concentration as well as to examine the behavior of PFOS and PFOA. This study aims for that, with a focus on Asia surface water environment.

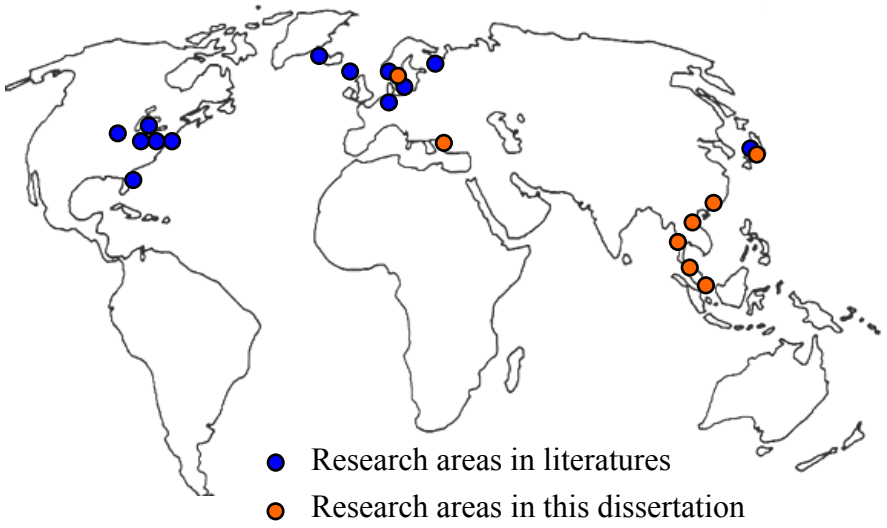


Figure 1.2 PFOS and PFOA in surface water: available research areas and research areas in this study (one point represents one country or one state for USA.)

I.1.3 PFOS and PFOA in drinking water

Due to persistent and bio-accumulative characteristics, appearance of PFOS and PFOA at certain levels in drinking water will pose a risk of human exposure to these chemicals. There is not yet safety levels of PFOS and PFOA set for drinking water in any countries except a state in USA, probably due to inappropriate number of scientific research and

information on PFOS and PFOA. Minnesota State of USA recommends safety concentrations of 0.5 μg/L for PFOA and 0.3 μg/L for PFOS in drinking water (MDH, 2007).

PFOS and PFOA concentrations in drinking water were rarely reported compared to those in surface water. A study in Japan indicated that there were levels in drinking water in an area that might cause an 25% increase of PFOS in human serum levels while exposing (Harada *et al.* 2004). The level of PFOS and PFOA is still questionable in majority of the world's drinking water.

I.2 RESEARCH OBJECTIVES

Based on the above background, this study has a goal to understand PFOS and PFOA contamination in various kinds of water from different locations and areas including those have not been studied before. Detail objectives of the study are:

1. To develop a method for quantification of PFOS and PFOA in environmental water.
2. To investigate distribution of PFOS and PFOA concentrations in surface water in certain areas in Japan, China, Vietnam, Thailand, Malaysia, Singapore, Sweden and Turkey.
3. To investigate PFOS and PFOA concentrations in wastewater treatment plant (WWTP) discharges in several areas.
4. To examine PFOS and PFOA concentrations in drinking water in Japan and other countries.
5. To examine relationship of PFOS and PFOA concentrations in drinking water with surface water in an area in general and with water supply source in particular.
6. To conduct mass flux analysis and search for sources of PFOS and PFOA in the areas where relatively high concentrations of PFOS and PFOA were found.

I.3 DISSERTATION STRUCTURE

The dissertation consists of seven chapters. Its structure in relation with overall research plan is shown in **Figure 1.3**. Following is a summary of each chapter content.

Chapter I is titled "*Introduction*". It gives a short research background, research objectives, research outlines, and the dissertation structure.

Chapter II is titled "*PFOS and PFOA: an Emerging Concern*". It is literature review chapter reviewing various aspect related to PFOS and PFOA.

Chapter III is titled "*Analysis of PFOS and PFOA in Environmental Water*". It includes a review on measurement method in literature and the method developed in this study for measurement of PFOS and PFOA.

Chapter IV is titled "*Water Sampling Surveys*". It gives overview of sampling campaign for water sampling surveys of water environment and tap water as well as protocol for sampling and sample pre-treatment.

Chapter V is titled "*PFOS and PFOA Pollution in Water Environment".* In this chapter, distribution of PFOS and PFOA in various surveyed areas are shown and discussed.

Chapter VI is titled *"Contamination in Tap Waters and Relationship to Surface Waters"*. In this chapter, concentrations of PFOS and PFOA in tap water are shown. Relationship with surface water and water sources are examined.

Chapter VII is titled "*Mass Fluxes Analysis"*. Mass fluxes were estimated and analyzed in a typical river system of Japan, and in Singapore in order to search for predominant sources of FPOS and PFOA.

Chapter VII, titled "*Conclusion and further study*", summaries all results obtained and proposes further study based on what are found.

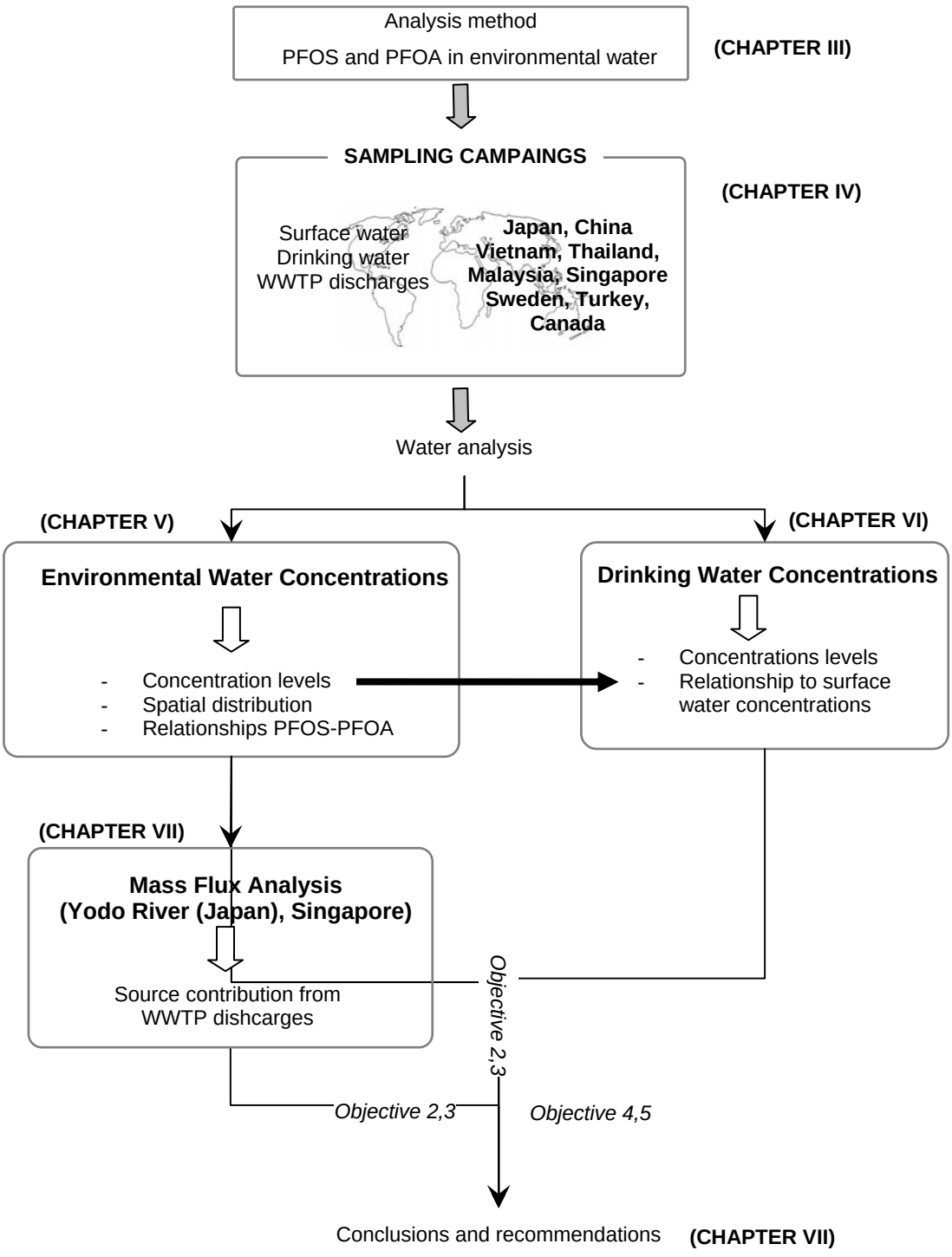


Figure 1.3 Schematic diagram of research plan and dissertation structure

CHAPTER II

PFOS AND PFOA: AN EMERGING CONCERN

II.1 INTRODUCTION

This chapter has objectives to give a short overview of information available on PFOS and PFOA in terms of (1) Physico-chemical properties and production methods (2) Production, use, and release to environment (3) Environmental fate, including POPs property and environmental levels, and (4) Toxicity. It would provide a glance at the problem of PFOS and PFOA as well as a necessary background for discussion in next chapters.

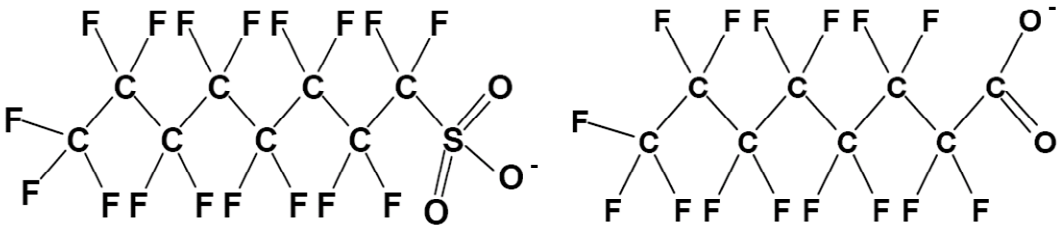
II.2 IDENTIFICATION OF PFOS AND PFOA

II.2.1 Chemical identities

PFOS and PFOA are fully fluorinated anion, which are commonly used as salts or incorporated in larger polymers. Their chemical structures are shown in **Figure 2.1**.

II.2.2 Physico-chemical properties

The physical and chemical properties of potassium salt of PFOS and PFOA free acid are listed in **Table 2.1**. Data are taken largely from the OECD hazard assessment (OECD,



Perfluorooctane sulfonate (PFOS) Perfluorooctanoate (PFOA)

Figure 2.1 Structural formulas of PFOS and PFOA

2002) and the 3M assessment (3M, 2003) for PFOS and USEPA (2002) for PFOA.

(1) ***Thermal behavior***

PFOS, which has air-water partition coefficient of less than $2x10^{-6}$, is essentially non-volatile, significantly less so than water, which has a Kaw of $2x10^{-5}$ (Henry's law constant of 0.044 Pa m3/mole). The reported vapor pressure of PFOA, 10 mm Hg, appears high for a low melting solid when compared to other low melting solids (3M, property, 2003). However, the vast majority of PFOA is consumed to make the ammonium or sodium salts (3M, USEPA, 2002). While it maybe expected that conversion of the PFOA acid to a salt should reduce its volatility, animonium salt of PFOA shows volatility at fairly low temperatures. The vapor pressure of animonium salt of PFOA was reported to be approximately $7x10^{-5}$ mm Hg at 20°C.

(2) ***Behavior in water***

PFOS and PFOA are both oleophobic and hydrophobic which means they tend to repel and not absorb water and oil.

The very low pKa value of PFOS acid (-3.27) indicates that PFOS will be present in water

Table 2.1 Physico-chemical properties for PFOA free acid and amonium salt of PFOS

Property	Potassium salt of PFOS	PFOA acid
Appearance at normal temperature and pressure	White powder	Liquid
Molecular weight (MW)	499 (for PFOS anion)	414
Melting point (MP)	> 400°C	45-50°C
Boilling point (BP)	Unable to determine	189-192°C / 736 mmHg
Vapor pressure (VP)	$3.31x10^{-4}$ Pa /20°C ($3.27x10^{-9}$ atm)	10 mmHg / 25°C (approx.)
Henry Law constant	$4.34x10^{-7}$/20°C	-
Solubility in pure water	519 mg/L (20 ± 0,5ºC) 680 mg/L (24 - 25ºC)	3.4 g/L
Solubility in pure octanol	56 mg/L	-
Air/water partition coefficient (K_{AW})	< $2x10^{-6}$	-
N-octanol/water partition coefficient (Kow)	Unable to measure	Unable to measure
Acid dissociation constant (for acid) (pKa)	- 3.27 (calculated)	2.5

Sources: OECD 2002, USPEPA 2005

environment completely in the ionized form (Brooke *et al.* 2004). Therefore, all property involving solution relate to the ionized from. The free acid of PFOA is expected to completely dissociate in water (leaving the anionic carboxylate in the water and the perfluoroalkyl chain on the surface). In aqueous solutions, individual molecules of PFOA anion loosely associate on the water surface and partition between the air/water interface (3M, property). Several reports note that PFOA salts self-associate at the surface, but with agitation they disperse and micelles form at higher concentrations.

Due to the surface-active properties of PFOS and PFOA and the test protocol itself, PFOS and PFOA forms multiple layers in octanol/water. Therfore, n-octanol/water (Kow) partition coefficients cannot be determined. 3M company determined the solubility of PFOS in octanol as 56 mg/l, and calculated the log Kow from the ratio of solubilities, giving a value of -1.08 (Brooke *et al.* 2004). Using the KOWWIN program, values of 4.13 is calculated for log Kow for the potassium salt, 6.28 for the acid, but the reliability of this program for substances of this type is unknown (Brooke *et al.*, 2004).

II.2.3 Origin of PFOS and PFOA

PFOS, PFOA and other perfluorinated compounds (PFCs) are man-made chemicals with no known natural occurrence. They also can be formed (by environmental microbial degradation or by metabolism by larger organisms) from related man-made fluorochemicals (see **2.4.1.3**)

In fact, PFOS and PFOA are members of a large family of perfluorinated substances - PFCs, which all have artificial origin (natural fluorinated compound contains only one fluorine atom). PFCs are composed of a carbon-fluorine chain and generally have side moieties such as carboxylic acids (PFOA acid) or sulfonic acids (PFOS acid) which are respectively called perfluorinated (perflooalkyl) carboxylates (PFCA) and perfluorinated sulfonates (PFCS) which makes up to major classes of PFCs (Giesy and Kannan 2002).

The carbon-fluorine bond in PFCs is very strong (110kcal/mol) and gives thermal and chemical stability to many PFCs. PFCs are manufactured not only because of that but also because of their special surface-active properties (Hekster *et al.* 2003). They repel both water and oil and act as surfactants, that is, they reduce surface tension and do so better than other surfactants (Renner 2001). These properties have led to the use of perfluorinated compounds in a wide variety of applications that will be discussed in detail in the section **2.4.1**.

PFCs are commercially produced by two major methods, telomerization (the process used to produce FTOHs) and electrochemical fluorination (ECF) **(14)**. Telomerization leads predominately to straight polyfluorinated chains, while electrochemical fluorination produces both linear and branched isomers.

(1) Production method for PFOS

The starting material for PFOS-related chemicals is perfluorooctanesulfonyl fluoride (PFOSF) that is manufactured through a Simons Electro-Chemical Fluorination (ECF). The main reaction equation is as follow.

$C_8H_{17}SO_2Cl + 18\ HF \rightarrow C_8F_{17}SO_2F + HCl +$ by products

PFOSF may be further reacted with methyl- or ethylamine to form *N*-ethyl- and *N*-methyl perfluorooctane sulfamide and subsequently with ethylene carbonate resulting in *N*-ethyl- and –methyl- perfluorooctane sulfamidoethanol (*N*-EtFOSE and *N*-MeFOSE). *N*-EtFOSE and *N*-MeFOSE were the principal building blocks of 3M's product lines. PFOS is formed after the chemical or enzymatic hydrolysis of PFOSF (3M, 1999).

Other production methods for perfluoroalkylated substances, telomerisation and oligomerisation. However, to which extent these methods are applied for production of PFOS and PFOS-related substances is not evident.

(2) Production method for PFOS

PFOA has been commercially manufactured by alternatively by ECF or telomerization process (USEPA, 2002). The 3M Company was reported to be largest manufacturer and importer of PFOA and its salts in the United States in 1999. They predominantly used the ECF process to produce a PFOA precursor which is ultimately converted to PFOA (80% linear). 3M is the only major company known to use the electrochemical fluorination process (Renner 2001). Other companies use a different process for the production of PFCs namely the telomerization process in which perfluoroalkylethylates are produced (Hekster *et al.* 2003, Renner 2001).

Telomerization has recently become more widely used in the production of many PFCs (So *et al.* 2004). The telomerization process also results in the production of fluorotelomer alcohols (FTOHs) which FTOHs have recently been shown to break down in the environment to form perfluorinated carboxylates (**see below**).

II.3 SOURCES

II.3.1 Production and use

PFCs have been produced five decades ago with a large of applications. PFOS and its related company has been ceased in 2000 while PFOA still produced.

II.3.1.1 Production and use of PFOS and PFOS- related chemicals

In 1997, 3M Company, the dominant producer of POSF (UNEP, 2006) reported the manufacture or importation into the United States of approximately 1,848 metric tons of POSF. For 2000, 3M forecasts a volume of 1,820 metric tons manufactured or imported into the United States. The global production of PFOSF by 3M until the production ceased is estimated to have been 13,670 metric tonnes (1985 to 2002), with the largest yearly production volume, 3700 metric tonnes of PFOS and PFOS related substances, in 2000 (UNEP, 2006).

PFOS and its related chemicals (mainly high molecular weight polymers in which PFOS represents a fraction of the total molecular weight) are used in a variety of products. These products can be divided into three main categories of use: surface treatments, paper protection, and performance chemicals. **Table 2.2** shows estimation of global production detail about production of PFOS-related chemicals by 3M Company.

PFOS and PFOS-related chemicals production and use after 2002

The major world producer of PFOS-related substances was 3M.. On 16 May 2000, 3M announced that the company would phase-out the manufacture of PFOS and PFOS-related substances voluntarily from 2001 onwards. By the end of 2000, about 90 % of 3M's production of these substances had stopped and in the beginning of 2003 the production ceased completely (UNEP, 2006). As a result, the level of use in many areas has decreased significantly over the last two or three years, in some cases to zero. Users have moved to alternative fluorine-based products (elomere based) in some areas, and to other technologies in other areas. The main areas where use is continuing at present are metal plating; semi-conductors; photographic; aviation; and fire fighting foams stock (Brooke *et al.* 2004).

PFOS and related chemicals or products containing them were still imported and/or manufactured in few countries of OECD in 2003 such as Canada, Germany, Italy, Japan, and Australia (OECD 2005). The volume PFOS and related chemicals were confidential in

many countries. For product containing PFOS and related chemicals, the total volumes was also imprecise but is likely to be at least 30 tons/year (OECD, 2005).

According to the recent submission from Japan to the secretariat of the Stockholm Convention, 2006, there is one manufacturer in Japan still producing PFOS and with a production amount of 1-10 tonnes in 2005 (UNEP 2006).

II.3.1.2 Production and use of PFOA and PFOA-related chemicals

3M has characterized its manufacture of PFOA and its derivatives in 1997 at less than 500,000 kg per year in the US, and its importation at less than 100,000 kg (3M Company, 2000a). Industry sources have characterized 3M as the dominant global producer of PFOA-related chemicals, manufacturing approximately 85 percent or more of total worldwide

Table 2.2 Use of PFOS and its related substances

Applications	**Global production (tons)**	**Detail applications**	**Related industry**
Surface treatment	2,160	Protection of apparel and leather, fabric/upholstery, and carpet	Textile mills, leather tanneries, finishers, fiber producers, and carpet manufacturers
		Aftermarket treatment of apparel and leather, upholstery, carpet, and automobile interiors	The general public or professional applicators
Paper protection	1,490	Food contact applications (plates, food containers, bags, and wraps)	Paper mills and, to some extent, converters who manufacture bags, wraps, and other products from paper and paperboard
		Non-food contact applications (folding cartons, containers, carbonless forms, and masking papers)	
Performance chemical	831	Fire fighting foams (*) Mining and oil well surfactants Acid mist suppressants for metal plating and electronic etching baths (*) Photolithography Electronic chemicals Hydraulic fluid additives Alkaline cleaners (*) Floor polishes (*) Photographic film Denture cleaners, Shampoos Chemical intermediates Coating additives Carpet spot, Cleaners Insecticide in bait stations (*)	Variety of specialized industrial, commercial, and consumer applications
Total	4,481		

volumes of the ammonium salt of PFOA (FMG, 2001, USEPA, 2002).

Companies which use this process include AsahiGlass (Japan), AtoFina (France), Clariant (Germany), Daikin (Japan) and DuPont (United States) (Hekster *et al.* 2003, Renner 2001). DuPont make perfluorooctanoic acid (PFOA) from which Teflon is made, a nonstick coating used for saucepans (ENDS 2003). PFOA is used also used to make Goretex (Renner 2003).

FTOHs are used as precursor molecules for the production of fluorinated polymers which, in turn, have similar uses to PFOS-based compounds such as in paper and carpet treatments (Dinglasan *et al.* 2004). They are also used in the manufacture of paints, adhesives, waxes, polishes, metals and electronics. The global production of FTOHs was estimated as 5 thousand tons during the years 2000-2002. 40% of the production occurred in North America (Dinglasan *et al.* 2004).

Results of a survey on production and use of PFCs in 2003 by OECD (2005) indicated that there is production of PFOA and related chemicals in US, EU, Japan while imported products were also available in other countries such as Canada, Australia (products containing PFOA or PFOA-related chemicals only). The amount of production/importation (tons) was confidential. It is noted that the total known trade in PFOA and related raw chemicals is likely to be between 100 and 200 tons/year, but possibly up to 800 tons/year in 2003. In Japan PFOA and PFOA-related chemicals are used in semiconductors, polymer production, and as surfactants.

According to USEPA (2002), aside from the US, OECD member countries that reportedly have production capacity include France, Germany, Italy, and Japan. There may also be some production in non-OECD countries such as China. Companies that may manufacture PFOA and its salts (3M Company, 2000b; Directory of World Chemical Producers, 1998; Dynax, 2000; Renner, 2001; SEMI, 2001) includes 3M Company, DuPont, Exfluor Research Corporation, PCR Inc. (United States); Ciba Specialty Chemicals, Clariant, Dyneon, Hoechst ktiengesellschaft (Germany); EniChem Synthesis S.p.A., Miteni S.p.A. (Italy); Asahi Glass, Daikin, Tohkem Products Corporation (Japan); Chenguang Research Institute of the Chemical Industry; Shanhai 3F New Materials Co., Ltd. (China).

Use of PFOA

PFOA acid is primarily used as a reactive intermediate, while PFOA salts are used as processing aids in the production of fluoropolymers and fluoroelastomers and in other surfactant use (USEPA, 2002). According to 3M, the vast majority of PFOA is consumed

to make the ammonium or sodium salts. 3M also uses PFOA as a reactive intermediate in the industrial synthesis of a fluoroacrylic ester. The fluoroacrylic ester is used in an industrial coating application (3M Company, 2000a). The salts of PFOA have additional uses, mostly in surfactant and emulsifier applications. These include the following:

Table 2.3 Use of PFOA acid and PFOA salts, and related-chemicals

Processing aid in the industrial synthesis of fluoropolymers and fluoroelastomers such aspolytetrafluoroethylene and polyvinylidene fluoride with a variety of industrial and consumer uses (3M Company, 2000a; DuPont, 2000; Daikin, 2001).
Post-polymerization processing aids in the stabilization of sus pensions of fluoropolymers and fluoroelastomers prior to further industrial processing (3M Company, 2000a)
Processing aid for factory-applied fluoropolymer coatings on fabrics, metal surfaces, and fabricated or molded parts (3M Company, 2000a)
Extraction agent in ion-pair reversed-phased liquid chromatography (Petritis, 1999)
Based on the physicochemical properties of the salts of PFOA, they may also have other related surfactant or emulsifier uses as a photographic chemical or in the manufacture of electroniccomponents such as semiconductors.

II.3.2 Environmental release

There is to date very limited information regarding their emissions and pathways to the environment. Since PFCs are not naturally occurring substances, their occurrence of PFCs in the environment is a result of anthropogenic manufacturing and use.

II.3.2.1 Direct sources

Direct releases of PFOS, PFOA are likely to occur during their whole life cycle. They can be released at their production, at their assembly into a commercial product, during the distribution and industrial or consumer use as well as from landfills and sewage treatment plants after the use of the products (3M, 2000). Due to their global production and application (see **2.3.1.1)**, release of PFOS and PFOA might occur in many part of the world. Dispersion of PFOS, PFOA is thought to occur through transport in surface water, or oceanic current and through living organism while, transport in air, adsorption to particles is less. The most non-biota environmental of concern is surface water.

An important source of PFOS and PFOA is through manufacturing in which sewage discharge might be discharged with high concentrations PFOS and PFOA residues. Supporting this, Hansen *et al.* (2002) indicated concentrations in Tennessee River USA

levelled up from an average 32±11ng/L to 114±19 ng/L for PFOS and from ND levels to 394±128 ng/L before and after a manufacturer in. In another case, ground water and drinking water around a Teflon manufacturer in Virginia, USA was found to contaminate with PFOA up to 10 μg/L (ENDS, 2004).

Another source of PFOS and PFOA is related with their industrial and commercial application. PFOS and PFOA are used to make fire-fighting foam (a significant portion of total PFOS). Their concentrations were high at fire-training places in Nevada, Florida, and Michigan states of USA, (Moody *et al.* 1999, 2002, 2003), in a fire extinguishing site in Tomakomai in Japan (Yamashita *et al.* 2004), at μg/L order. The use of PFOS in semiconductor industry is estimated to result in a realest of 43 kg/year in the EU while PFOS released in the USA from semiconductors is estimated to be in the same range (UNEP, 2006). Prevedious *et al.* 2003 estimated that that the majority (~80%) of PFCAs, which includes PFOA, has been released to the environment from fluoropolymer manufacture and use.

II.3.2.2 Indirect sources

There were data showing that both PFOS and PFOA can be formed through degradation of related substances those are PFCs produced by either by ECP or by fluorotelomer process. The numbers of study were very limited; therefore the rate and extent of those formation are presently unknown.

Tomy *et al.* (2004) found that N-ethyl perfluorooctanesulfonamide (N-EtPFOSA) is a precursor of PFOS in fish. Martin *et al.* (2004), suggested that atmospheric *N*-EtPFOSA (and PFOSA) can be sources of environmental PFOS. There are other compounds similar in structure to *N*-EtPFOSA that may also be neutral PFOS precursors in fish. It was also recommended that perfluorosulfonamido alcohols might also be contributing to loadings of PFOS in remote regions (Martin *et al.,* 2004).

Ellis *et al.* (2004) and Dinglasan *et al.* (2004) indicated that fluorotelomer alcohols (FTOHs), a product of telomerization process used to produce PFOA, can be broken down either in the atmosphere or in living organism to from perfluorinated carboxylates (PFCAs) including PFOA (respectively). Under an atmospheric laboratory condition, it was showed that 8:2 FTOH degrading approximately 5% to a homologous series of PFCAs in which 1.5% were PFOA (Ellis *et al.* 2004). Aerobic degradation of 8:2 FTOH could form telomere acids and ultimately produced the highly stable PFOA (Dinglasan *et al.* 2004).

The appearance of PFOS and PFOA far from anthropogenic sources supports these indirect sources of PFOS and PFOA. This will be discussed detail in section **2.4.1.3**. Previdous *et al.* (2005) commented that although indirect sources were estimated to be much less important than direct sources, there were larger uncertainties associated with the calculations for indirect sources.

II.4 ENVIRONMENTAL FATE

II.4.1 POP's characteristics of PFOS and PFOA

Persistent organic pollutants (POPs) is a group of pollutants set by the Stockholm Convention (2001) in response to the urgent need for global action to protect human health and the environment from chemicals that are (1) highly toxic, (2) persistent, (3) bio-accumulative and (4) moving long distance in the environment. Recently, PFOS have been reviewed in a report of the Persistent Organic Pollutants Review in Stockholm Convention (UNEP 2006). This section discusses the first three POP's characteristics of not only PFOS but also PFOA for comparison purpose. Toxicity will be discussed in section **2.4.4**.

II.4.1.1 Persistence

The stability that makes PFCs desirable for commercial use also makes them potentially significant environmental contaminants due to their resistance to natural breakdown processes, that is, their persistence (Key *et al.* 1997). PFOS and PFOA are extremely persistent. They does not hydrolyse, photolyse or biodegrade in any environmental condition tested (OECD, 2002, USEPA, 2002).

PFOS half-life in water was set to be greater than 41 years while its indirect photolytic half-life of PFOS at 25^{o}C was calculated to be more than 3.7 years (UNEP 2006). Hydrolytic half-life of PFOA acid was estimated greater than 97 years (3M 2001). Amonium salt of PFOA half-life was estimated to be greater than 349 days, using the iron oxide (Fe2O3) photoinitiator maxtrix model (USEPA 2002).

PFOS is the end product of other perfluorinated substances. It was predicted that of 171 studied perfluorinated substances, over 99% would biodegrade to extremely persistent perfluorinated acids. Of them, 109 susbtances were predicted to end up as perfluorinated sulfonic acids, including PFOS, and 61 as perfluorinated carboxylic acids (Dimitrov. *et al.*, 2004)

Table 2.4 POPs characteristics of PFOS (UNEP, 2006)

Criterion	Meets the criterion	Remark
Persistence	Yes	Extremely persistent. No degradation recorded in chemical or biological tests
Bioaccumulation	Yes	Found in highly elevated concentrations in top predators. Calculated hypothetical BMFs = 22 - 160. BCF in fish = 2796 - 3100.
Potential for Long-Range Environmental Transport	Yes	Atmospheric half life > 2 days (estimated value based on photolytic half life > 3.7 years)
Toxicity	Yes	Sub-chronic exposure: Mortality in monkeys at 4.5 mg/kg bw/day. Reproductive toxicity: mortality in rat pups at 1.6 mg/kg bw/day. Acute toxicity to Mysid shrimp (Mysidopsis bahia): LC50 (96h) = 3.6 mg/L Acute toxicity to fish, Fathead minnow (Pimephales promelas): LC50 = 4.7 mg/L1

II.4.1.2 Bio-accumulation

Bio-accumulation is the ability of a substance to accumulate in living tissues to levels higher than those in the surrounding environment, expressed as the quotients between he concentration in the target tissue and the environmental concentration. Probably because of both hydrophobic and lipophobic characteristics, PFOS do not accumulate in fatty tissues of the body but instead binds preferentially to proteins in the plasma (Kerstner-Wood *et al.* 2003), and in the liver (Luebker *et al.* 2002). This is different from typical persistent and bioaccumulative environmental pollutants.

In another study on fish, the common shiner, the bioaccumulation factor for PFOS was reported to vary between 6,300 and 125,000 (see Hekster *et al.* 2003). (Taniyasu *et al.* 2003). Bioconcentration factors for PFOS in livers of fish were estimated from the results for two species of marine fish and one freshwater species. Bioconcentration factors for PFOS ranged from 274 to 41,600. (Martin *et al.* 2003a). UNEP 2006 commented that when strictly look at the BCF values, it is clear that these values are below the numeric BCF criteria in Stockholm Convention Annex D (the reported BCF values are below 5000) but, in this particular case, as noted above, the BCF numeric criteria may not adequately represent the bioaccumulation potential of the substance. Monitoring data from top predators at various locations show highly elevated levels of PFOS (see **2.4.3.2**) and demonstrate substantial bioaccumulation and biomagnification (BMF) properties of PFOS.

It is notable that the concentrations of PFOS found in livers of Arctic polar bears exceed the concentrations of all other known individual organohalogens (Martin *et al.*, 2004a).

For PFOA, available data on its bioaccumulation potential showed it slightly bio-concentrated. BCFs were 1.8 in Fathead minnows exposed to 25mg/L of ammonium salt of PFOA for 13 days (Howell *et al.* 1995), 3.1-9.1 in carp exposed to 5 g/L and 50 g/L (Kurume Laboratory, 2001). The GM (GSD) of the BCF of PFOA was 3.2 (7.9) in turtles exposed to concentration of 16.7-87,100 ng/L PFOA in a river in Japan (Morikawa *et al.*, 2006)

II.4.1.3 Long-range environmental transport

PFOS has been measured in a wide range of biota in the Northern Hemisphere such as the Canadian Arctic, Sweden, the US and the Netherlands and in the vast majority of the species examined. The presence of PFOS in Arctic biota, far from anthropogenic sources, demonstrates the potential of PFOS for long-range transport.

The mechanisms of the long-range transport are not known. PFOS itself is not expected to volatilise significantly (see **2.2.2**), therefore assumed to be transported in the atmosphere predominantly bound to particles, because of its surface-active properties, rather than in a gaseous state. In another hand, the appearance of PFOS far from anthropogenic sources could also be due to the transport of volatile PFOS-related substances that eventually

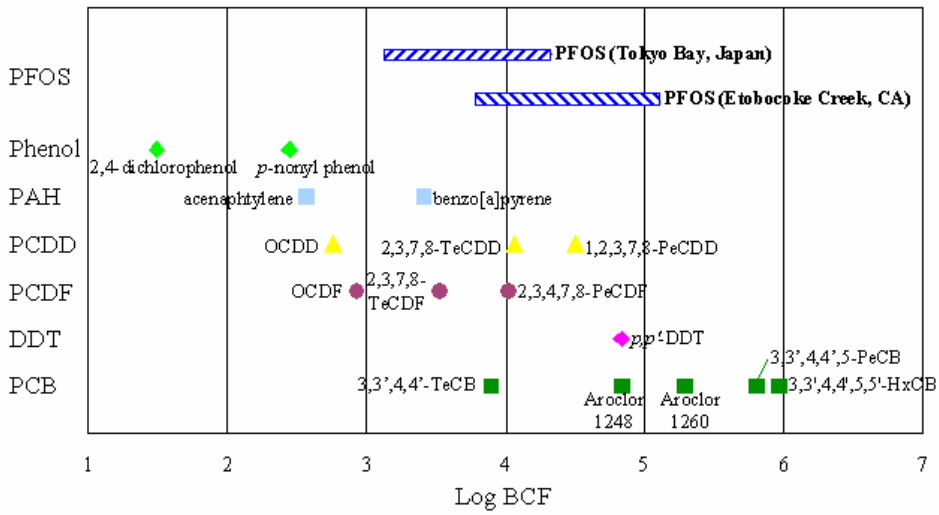


Figure 2.2 Bioconcentration factor (BCF) of PFOS and the other pollutants (Taniyasu, 2002)

degrade to PFOS.

Some of the PFOS-related substances have a considerably higher vapour pressure than PFOS itself, and are as a result more likely to be volatile. The vapour pressures of precursors, such as N-EtFOSEA and N-MeFOSEA, may exceed 0.5 Pa (1000 times greater than that of PFOS) (Giesy and Kannan 2002). Other potential precursors of PFOS considered volatile include N-EtFOSE alcohol, N-MeFOSE alcohol, N-MeFOSA and N-EtFOSA (3M, 2000).

Similarly to PFOS, PFOA has been found in Northern Hemisphere, far from anthropogenic sources, even thought with the frequency of occurrences and the concentrations less than those of PFOS (see **2.4.3.2**). Prevedious *et al.* 2006, suggested that in addition to atmospheric transport/degradation of precursors, atmospheric and ocean water transport of the PFCAs themselves could significantly contribute to their long-range transport. It was estimated that 2-12 tons/year of PFOA are transported to the Artic by oceanic transport, which is greater than the amount estimated to result from atmospheric transport/degradation of precursors.

II.4.2 Levels of PFOS and PFOA in water environment

The most non-biota environmental compartment of concern for PFOS and PFOA is water because these compounds have moderate water solubility (see **1.2**), while atmospheric PFOS and PFOA might be not as such concern because of their involatile characteristic (see **1.2**). However, in comparison with data in biota, data of PFOS and PFOA concentrations in water were less.

II.4.2.1 Water environment near fluorochemicals manufacturing and AFFF application sites

High levels of PFOS and PFOA were often found near fluorochemicals manufacturing and AFFF application sites at high ng/L levels to ug/L levels. They are essentially significant point sources. According to USEPA 2002 and OECD 2002, its has been reported concentrations of PFOS and PFOA in surface water around 3M facility at Decatur, AL (Giesy, 2001e), in which concentrations in two out of three downstream water were found significantly greater than the two upstream sites. Concentrations were 50 ug/L and 82 ug/L PFOS 1,900ug/L and 1,024 ug/L PFOA in downstream water while 9-53 ng/L PFOS and 8-28 ng/L PFOA were measured at the upstream water. Hansen *et al.* (2002) indicated concentrations in Tennessee River (USA.) levelled up from an average 32±11ng/L to 114±19 ng/L for PFOS and from ND levels to 394±128 ng/L before and after a the

fluorochemical manufacturing facility at Decatur AL (the 3M facility mentioned above). The report found that consistency of concentration over upstream sites and over downstream sites and suggested the absence of either major environmental sinks or additional sources in the areas sampled.

Moody *et al.* (1999) monitored ground water collected in two fields where fire-training activities had frequently occurred (one in Nevada and another in Florida) and found perfluorinated carboxylates containing 6 to 8 carbons with total concentration ranging from 125-7090 μg/L in which PFOA ranging 45-6570 μg/L. Moody *et al.* (2003) found groundwater from wells around a fire-training area at Michigan, USA containing four perfluorinated surfactants including PFOS and PFOA ranging in concentration from 3 to 120 μg/L. It was remaked that the detection of perfluorocarboxylates at field sites after 7-10 years of inactivity indicates their potential utility as markers for delineating groundwater impacted by firefighting activity.

Following an accidental release of fire-fighting foam into Etobicoke Creek (Canada), it was reported the concentrations of PFOS and PFOA in surface water sampled upstream and downstream of the spill location. Downstream surface water samples taken over the three week period post-spill had PFOA levels of 0.035-10.6 μg/L and PFOS levels of 0.16-995 μg/L while corresponding downstream levels of 0.008-0.033 ng/L and ND respectively (Moody *et al.* 2002).

II.4.2.2 General surface water

U.S.A.

3M's Multi-City Study reported on PFOS and PFOA concentrations from various samples collected in six cities of USA (3M, 2001a). in which four cities (Decatur AL, Mobile AL, Columbus GA, Pensacola FL) have manufacturing or industrial use of fluorochemicals; and two cities (Cleveland TN, Port St. Lucie FL) do not have significant fluorochemical activities. Across all cities, PFOS concentration ranges were 41-5,290 ng/L (POTW effluent); <2.5-63 ng/L (drinking water), <2.5-53,100 ng/L (landfill leachate), <2.5-138 ng/L (surface water) and <2.5-2,930 ng/L (quite water). PFOA concentration ranges were. 40-2,420 ng/L; ND-29 ng/L; ND-48,100 ng/L; ND-83 ng/L; ND-97 ng/L respectively. It is noted that the samples from generally inhabited the lower end of the above ranges.

PFOS and PFOA were also found ubiquitous in New York State surface water with median of 1.6-6.4 ng/L for PFOS and 14-49 ng/L for PFOA (Simcik *et al.*, 2005). The compounds

were detected in Michigan State water with mean concentrations ranged of 1.8-17 ng/L PFOS and 4.4-22 ng/L PFOA (Sinclair *et al.*, 2004, Kannan *et al.*, 2005).

Japan

The first environmental survey of PFOS and related substances in Japan (Taniyasu *et al.* 2002) found the highest concentration in surface water in Tokyo Bay at 59 ng/L (mean: 26 ng/L). The concentrations of PFOS in surface water were similar to those of polyaromatic hydrocarbons (PAHs) and much higher than those of PCBs, dioxins and furans (Taniyasu *et al*, 2002). Fresh water concentrations in Lake Biwa was reported at 7.4 ng/L.

Saito *et al.* (2003, 2004) determining the PFOS and PFOA concentrations in surface water samples from various regions in Japan found a large geographical difference in concentrations. The geometric means of concentrations for different regions were reported from 0.9 to 14.9 ng/L for PFOS and 1.0-21.5 ng/L for PFOA and the overall range was 0.24-37.32 ng/L for PFOS and 0.1-456 ng/L. To search for the sources, it was found exceptionally high concentrations at several hundreds ng/L for PFOS and up to μg/L level for PFOA in Osaka (Saito *et al.*, 2004, Tanaka *et al.*, 2006). The authors comment that the levels are much lower than those reported for the US, with the exception of two rivers where concentrations of 135 and 157 ng/L were measured.

Nordic Europe

A screening on distribution of perfluorinated alkylated substances (PFAS) in the European Nordic environment (Berger *et al.*, 2004) revealed PFOA as the predominant PFAS in water samples collected. The medians of PFOA concentration were 7.8 ng/L for lake water, 20.5 ng/L for sewage discharge, and 297 ng/L for landfill effluent while PFOS concentration medians were less than 1 ng/L, 12.7 ng/L and 65,8 ng/L respectively.

II.4.2.3 Drinking water

Ground water and drinking water around a Teflon manufacturer in Virginia, USA was found to contaminate with PFOA up to 10 μg/L (ENDS 2004a, Allopp). Drinking water samples in Japan were contaminated at maximum concentration of 40 ng/L for PFOA in Osaka area (Saito *et al.* 2004) and at about same level for PFOS in Tokyo (Harada *et al.* 2003). Both authors indicated that the sources of tap water area from surface water which were contaminated at the same levels of PFOS and PFOA concentration.

A recent study of surface water and tap water in Ruhr (Germany) (Skutlarek *et al.* 2006) found drinking water contaminated up to 519 ng/L for PFOA and 22 ng/L for PFOS. The author comment that the concentrations found in drinking waters decreased with the concentrations of the corresponding raw water samples along the flow direction of the Ruhr river (from east to west) and were not significantly different from surface water concentrations. This indicates that perfluorinated surfactants are at present not successfully removed by water treatment steps.

II.4.3 Levels of PFOS/PFOA in biota

II.4.3.1 In human

PFOS and PFOA do not accumulate in lipids of the body, but instead, blood and liver of wildlife. PFCs may not be as prevalent in human milk as in blood (Kuklenyik *et al.*, 2004). Concentrations of PFOS in whole blood, serum and plasma of general population of various countries are summarized in **Table 2.5**. PFOS concentration both within and between the different countries is quite variable, however mean levels fluctuated from several to several tens ng/mL, lowest in India (<3 ng/mL) and highest in USA and Poland

Table 2.5 Accumulation of PFOS in human blood

Country	Number of samples	Concentration (ng/mL)		Matrix	Reference
		Mean	Range		
USA. (Michigan, Kentucky and New York)	*N*= 175	49.5	<1.3-164	Sera	*
USA, Atlanta	*N*= 20	NA	3.6-164	Sera	Kuklenyik, 2004
USA	*N*= 645	34.9	<4.3-1656	Sera	Olsen, 2003
Northern Canada	NA	36.9	2.8-57.9	Blood plasma	Tittlemier, 2004
Colombia	*N*= 56	8.2	4.6-14	Sera	*
Brazil	*N*= 27	12.1	4.3-35	Sera	*
Italy	*N*= 50	4.3	<1-10.3	Sera	*
Poland	*N*= 25	44.3	16-116	Sera	*
Belgium	*N*= 20	13.9	4.5-27	Blood plasma	*
Sweden	*N*= 66	18.2	1.7-37	Whole blood	Karrman, 2004
India	*N*= 45	2.0	<1-10.3	Sera	*
Malaysia	*N*= 23	12.4	6.2-18.8	Sera	*
Korea	*N*= 50	21.1	3.0-92	Sera	*
Japan	*N*= 38	17.1	4.1-40.3	Sera	*
Japan	*N*= 26	8.1	2.0-20.2	Whole blood	Masunaga, 2003
Japan	*N*= 10	9.0	2.4-14	Whole blood	Taniyasu, 2003

*Notes: * Kannan et al. 2004, NA: not available*

(>30 ng/mL). Kannan *et al.* (2004) remarked that concentration and frequency of occurrence of other PFCs in serum samples (in ten countries listed in the table) including PFOA, PFHxS, PFOSA, were relatively lower than PFOS. Serum PFOA concentration were generally 2 to 7 fold lower than PFOS concentrations with an exception of Korean samples (Kannan *et al.,* 2004). However, a study in Sri Lanka (Guruge *et al.,* 2004b) reported levels of PFOA in human serum (0.24ng/mL) were higher than those of PFOS (0.13ng/mL).

Changing form urban to local, levels of PFCs including PFOS and PFOA in human blood in Sri Lanka was significantly reduced (Guruge *et al,* 2004). For examples, level of PFOS was 10-fold higher in urban area. In terms gender, the effect on PFCs concentration might be not conclusive since some researchers reported concentrations in males was significantly than female (same observation for the other POPs such as PCBs and dioxins) while Kannan *et al.* (2004) reported there is no difference between levels in male and females in 10 countries listed above.

PFOS and PFOA were also quantified in occupationally workers. Olsen *et al.* (1999) conducted studies on PFOS concentration in blood samples from workers in a fluorochemical production in Belgium in 1995 (*N*=178) and in 1997 (*N*=145). The mean (range) serum concentrations in μg/L were 2,190 (from 0 to 12830) and 1,750 (from 100 to 9,930) in two years respectively. In another study (Olsen *et al.*, 2000), PFOA was measured in workers (*N*=74) involved in the production of ammonium salt of PFOA at the concentration range (mean) of 6,400 (100-81,300) μg/L. Therefore, those mean PFOS and PFOA levels in occupationally population are considered two to three orders of magnitude higher than those in general population as shown in **Table 2.5**.

II.4.3.2 In other living organisms

PFCs have been detected in various living organisms including fish, birds, and mammals and from various locations as shown in **Table 2.6**. Mean concentrations of PFOS in the whole body homogenates of the fish were 450, 110, 46 ng/gWW for sculpin, smelt, and alewife respectively in Lake Ontario (USA) while concentration in blood and liver range from 33-384 ng/g and 3-310 ng/g in different species of fish in Lake Biwa (JP). Berger et al, 2004 indicated that PFOS was the predominant PFCs in Nordic countries. Martin *et al.*, 2004b found PFOSA in fish liver at similar concentrations to PFOS (ranging of PFOS from 5.7-50g/g for PFOS, and 2.0-18ng/g for PFOSA). One author denoted that PFOS was the predominant PFCs while the others reported PFOA was below the detection limits (Sinclair *et al.*, 2004, Martin *et al.*, 2004b). PFOA were also detected in Lake Ontario and Nordic

countries. Following PFOS, PFOSA were measured at high concentration in fish as reported by Berger *et al.*, 2004 and Martin *et al.*, 2004b. PFOS and other PFCs was not only detected in freshwater fish but also marine fish. Berger *et al.* 2004 found a high variability in PFCs levels reflecting differences in tropic levels. Similar to fresh water fish, PFOS was the predominant compounds. PFOS were detected in the majority of samples. Kannan *et al.* 2002 indicated that PFOA was not found in any of the fish samples above the limits of detection in Italian coast.

PFOS has been found in birds from USA, the Canadian Artic, from Italian and Japan (respectively Kannan *et al.* 2001a, Martin *et al.* 2004b, Kannan *et al.* 2002a, and Taniyasu *et al.*, 2003). It was detected PFOS in bood and liver and eegs of the birds. For examples, the concentration for birds form the Great Lakes region ranged from <1 to 2030 ng/ml in blood plasma and <12-1780 ng/gWW in liver tissues. Holmtron *et al.* 2005 measured PFOS in guillemot eggs during 1968 and 2003 showing that there was an increasing concentration of PFOS from 25ng/gWW in 1968 to 614 ng/gWW in 2003.

PFCs, especially PFOS, have been found in marine and terrestrial mammals, from a wide range of geographical region. Kannan *et al.* 2001b detected PFOS in tissues from marine

Table 2.6 Appearances of PFOS and PFOA in various animals of the food chain

Species	**Locations**	**Matrix**	**Predominant compounds**	**Reference**
Freshwater Invertebrates and Fishes	Great Lakes (USA), Japan, Canadian Artic, Nordic Countries	Whole body, blood, liver	PFOS	Taniyasu 2003; Martin 2004a, Martin 2004 b), Sinclair 2004, Berger 2004,
Marine Fish	Japan, Nordic countries, Mediterranean, Gulf of Mexico, Chesapeake Bay (USA)	Blood and liver	PFOS	Taniaysu 2003, Berger 2004, Kannan, 2002a), Kannan, 2002b),
Birds	USA, Canadian Artic, Italy and Japan and Korea, Baltic	Liver, blood	PFOS	Kannan 2001, Martin 2004, Kannan 2002a)c) and Taniyasu 2003, Holmstrom, 2005
Amphibians	USA	Liver	PFOS	Giesy 2001
Marine Manmals	USA (East and West), Alaska, Northern Baltic Sea, the Arctic (Spitsbergen) and Sable Island in Canada, Northern Europe, Mediterranean, North Sea,	Blood and liver	PFOS	Kannan 2001b), Kannan 2002a), Van de Vijver *et al.* 2004),
Terrestial and Aquatic Manmals	Canadian Arctic, USA (various locations), Japan	Liver and blood	PFOS	Kannan 2002d), Martin et al 2004, Guruge 2004a)

mammals from the east and west coast of the US, Alaskan coastal waters, the northern Baltic Sea, the Arctic (Spitsbergen) and Sable Island in Canada. PFOS were also detected in liver of polar bear (Martin *et al.* 2004, Kananan *et al.* 2004). Notably, at the mean levels of 3100 ng/g of PFOS found in livers of arctic polar bear in Canadian Arctic, PFOS concentration exceeds the concentrations of all other known individual organohalogens (Martin *et al.,* 2004). PFOA were detectable but at lower concentrations, ranging from 2.9 to 13 ng/g. Polar bear is at the top of a food chain and would therefore be expected to contain comparatively high levels of PFOS.

For terrestrial and aquatic mammals, PFCs, especially PFOS were found in Canadian Artic foxes (Martin *et al.*, 2004b) , mink, otter in USA (Kannan *et al.*, 2002d), beef cattle in Japan (Guruge *et al.* 2004). Mink are top carnivores in aquatic ecosystems and otters are top predators of riverine food chains. A study from various locations across the USA (Kannan *et al.* 2002d) found comparatively high concentrations of PFOS (20 to 5140 ng/gWW) in mink and otter livers (25ng/g to 294ng/gWW). PFOA and the other PFCs (PFOSA, PFHxS) were detected in some of otters and minks though generally at lower concentration than PFOS. Maximum concentrations for FOSA were 590 ng/g, for PFHxS, 85 ng/g, and for PFOA, 27 ng/g in mink. The author also indicated that concentration of PFOS were again greatest in animals that were collected from more urbanized areas suggesting that urbanized areas are the primary sources of fluorochemicals to the environment.

II.5 TOXICITY AND HEALTH RISK CONCERNS

II.5.1.1 Eco-toxicity

PFOS has shown moderate acute toxicity to fish and aquatic invertebrates. The lowest observed median lethal concentration LC_{50} (96h) was estimated to be 4.7 mg/l and 3.6 mg/l for lithium salt of PFOS, in fathead minnow (*Pimephales promelas*) and the mysid shrimp (*Mysidopsis bahia)* respectively (OECD 2002). The lowest NOEC, 0.3 mg/l and 0.25 mg/l have been observed in the two species respectively (OECD, 2002). In another study (MacDonald *et al.* 2004), midge larvae (*Chironomus tentans*) did not survive exposure to 100 µg/l in the water. At doses of 50 µg/l or greater, there was a significant reduction in midge survival, a significant decline in growth and adverse impacts on emergence of adult midges from larvae. Median lethal concentration LC_{50} was 45.2 µg/L, much lower than those of the two species mentioned above. Although the adverse effects on midges in this study occurred at concentrations that still normally exceed environmental concentrations (see above), higher concentrations of PFOS have been reported in the environment

following accidental spills of PFOS, and this brings into concern possible adverse impacts on aquatic midges.

Available studies on toxicity of PFOA on aquatic organism showed that PFOA might not as sensitive as PFOS. For examples, on midge larvae, a similar test to PFOS for PFOA indicated no significant impacts on survival or growth. In another study on fathead minnow (*Pimephales promelas*) (Oakes *et al.* 2004), exposure to water concentrations of 0.3-100 mg/L did not cause an increase in mortality of the fish, however, some adverse effect were observed in female fish at PFOA concentration above 30 mg/L. A study was conducted on the toxicity of PFOA on zooplankton communities set up in the laboratory (Sanderson *et al.* 2003). The introduction of PFOA at concentrations of 10 and 70 mg/l caused the structure of the ecosystem to change. The study suggested that further investigations needed to be carried out to test environmentally relevant concentrations of PFOA on freshwater ecosystems.

II.5.1.2 Toxicity to mammals

A study on rats showed that the lowest dose at which weight loss occurred in the animals after giving PFOS was 0.4 mg/kg/day (the lowest observed adverse effect level or LOAEL) (Renner 2001← Christian *et al.* 1999). This corresponded to a liver concentration of 58 ppm. In wild mink, the greatest concentration that was found in livers was 6 ppm (see 2.4.3.2). Mink could be more or less sensitive to PFOS than rats, so it is possible that current environmental levels of PFOS may already be causing adverse effects in such wildlife species (Renner 2001). According to Renner (2001), the US Environmental Protection Agency conducted a study on rhesus monkeys which showed that no monkeys survived beyond 3 weeks into treatment with PFOS at a dose of 10 mg/kg/day. At a dose of 4.5 mg/kg/day, no monkeys survived beyond 7 weeks into treatment. A study on cynomolgus monkeys showed they died at doses as low as 0.75 mg/kg/day. There were also changes in the livers of the monkeys and significant reductions in blood cholesterol.

PFOA has been shown to be a strong tumour promoter, showing a 56% tumour incidence in 12 months of dietary exposure at 0.02% (w/w) (Adinehzadeh *et al.,*1999). Another long term feeding study showed that PFOA exposure at 300 ppm in the diet over 2 years increased cancers of the liver (liver adenomas) and pancreas (pancreatic acinar cell adenoma) (Olsen *et al.,* 1998).

Adverse effects in mammals have been shown on liver by PFOS and PFOA (Kawashima *et al.,* 1995; Berthiaume and Wallace 2002); on immune system by PFOA (Yang *et al.,* 2001,

2002) on development (Lau *et al.*, 2004) and neuroendocrine system by PFOS (Austine *et al.* 2003). Austine *et al.* 2003 investigated the effects of PFOS on the neuroendocrine system in adult female rats. PFOS was shown to disrupt the regularity of the estrous cycle PFOS at a dose of 1 or 10 mg/kg body weight for 2 weeks and this indicated that PFOS can function as an endocrine disruptor. Importantly, it was noted that the low dose of PFOS that was given which affected the estrous cycle was lower than levels present in wildlife. Levels in the serum of the treated rats were also similar to levels in humans who had been occupationally exposed to PFOS. Binding to blood proteins might be one of the reason for endocrine disruption. However Jones *et al.* (2003) found that PFOS bound to protein at extremely high concentrations in fish and bird that were normally not found in them.

II.5.1.3 Toxicity to human

Alexander *et al.* (2003) evaluated the mortality of male and female workers (*N*=2083) who had been employed for at least one year at a facility that produced perfluorooctanesulphonyl fluoride (POSF)-based fluorochemicals. Results showed the risk of death from bladder cancer was increased for the entire cohort. It was also concluded that workers employed in high exposure jobs (based on biological monitoring data for PFOS) had an increased number of deaths from bladder cancer. However it is not clear whether these cases (3 cases among 134 deaths among 2083 workers) can be attributed to fluorochemical exposure, an unknown bladder carcinogen encountered during the course of maintenance work, and/or non-occupational exposures. With only three observed cases, the possibility of a chance finding can not be ruled out. In addition, the study also showed two deaths from liver cancer in the workers with at least one year of high or low exposure to PFOS. These results were of interest because studies on laboratory rodents show that the liver is the primary target organ for PFOS.

Another study on mortality was conducted on individuals who were occupationally exposed to PFOA (Gilliland and Mandel 1993). The risk of mortality from prostate cancer was increased with increasing duration of work for those in jobs exposed to PFOA. The study suggested that because there were only a small number of cases, the results should be interpreted cautiously since the increase in prostate cancer deaths could be due to other factors. Further research on prostate cancer risk from PFOA exposure was suggested.

Several studies have been related to a DuPont manufacturer of Teflon in West Virginia. DuPont produces Teflon from PFOA. It reported there was a statistically significant excess of prostate cancer and female reproductive cancers in local residents the manufacturer compared with the US average. In addition, examination of health certificates of 5000 of

the DuPont employees showed an excess of other cancers such as non- Hodgkins lymphoma, leukaemia and multiple myeloma (ENDS 2004a). However, according to another study commissioned by DuPont to investigate health of its employees at the plant (see ENDS 2004a), no excess risk of cancer was found but there was a slight (about 10%) increase in serumcholesterol and also a rise in serum triglycerides among some individuals who had serum PFOA levels of greater than 1000 ppb (DuPont 2005).

CHAPTER III

ANALYSIS OF PFOS AND PFOA IN EVIRONMENTAL WATER

III.1 INTRODUCTION

This chapter has two objectives. Firstly, it is to review the method for quantification of PFOS and PFOA in environmental water available in literature during 1999-2005. The period before that, measurement of PFOS and PFOA was rarely conducted. Secondly, it is to show the method developed for quantification of PFOS and PFOA in this study, which is directly related to the following chapters in this dissertation (Chapter V, VI, VII).

III.2 AN OVERVIEW OF PFOS AND PFOA MEASUREMENT METHOD

Table 3.2 summaries methods for analysis of PFOS and PFOA in environmental water. LC/MS and LC/MS/MS were the most common analytical technique for quantification of PFOS and PFOA. GC/MS and GC/MS/MS and ^{19}F NMR (Moody 1999) were rarely used in measurement of PFOS and PFOA.

In order to quantify the trace levels of PFOS and PFOA (ng/L orders), water concentration (extraction) is needed. Direct measurement without concentration by ^{19}F NMR and ES-MS, have been demonstrated for PFOS (Moody *et al.*, 2001-1003), however, the detection limits were relatively high, at 3-10 μg/L. The most common used method of extraction is solid phase extraction (SPE) which normally apply reversed phase cartridge. Reversed phase separations involve a polar or moderately polar matrix (mobile phase) and a non-polar stationary phase. The analyte of interest is typically mid-to nonpolar.

Retention of organic analytes from polar solutions (e.g. water) onto SPE material is due primarily to the attractive forces between the carbon-hydrogen bonds in the analyte and the functional groups on the SPE material surface. These nonpolar-polar attractive forces are van der Waals forces or dispersion forces. To elute an adsorbed compound form a reserved phase, SPE tube or disk, a non-polar solvent was apply to disrupt the forces that bind the compound to the packing.

Table 3.1 A summary of analysis method for PFOS and PFOA in environmental water

Author	Extraction method	Quantification method	LOD and LOQ for PFOS	LOD and LOQ for PFOA
Hansen 2002	SPE: Sep-pak C18 cartridge	HPLC-ES/MS/MS	LOD = 5 ng/L LOQ = 10-25 ng/L	LOD = 25 ng/L LOQ = 25-50 ng/L
Taniyasu, 2003	SPE: Sep-pak C18 cartridge	HPLC-MS	LOD = 4 ~ 9 ng/L	-
Saito 2003, 2004, Harada 2003, Morikawa 2005	SPE: Pre-sep C Agri cartridge	HPLC-MS	LOD = 0.06 ng/L LOQ = 0.1 ng/L	LOD = 0.04 ng/L LOQ = 0.1 ng/L
Simcik 2005	SPE: C18 cartridge (Sulpeco)	LC/MS	LOQ >= 0.28 ng/L	LOQ >= 0.29 ng/L
Boulanger 2004, 2005	SPE: C18 cartridge	HPLC-MS (MSD)	LOQ = 0.7 ng/L	LOQ = 13 ng/L
Moody 2001, 2002	SPE: C18 cartridge	HPLC-MS/MS	LOQ = 17 ng/L	LOQ =9 ng/L
Loewen 2005	SPE: C18 silica gel colume	HPLC-ES/MS/MS	LOD = 0.39 ng/L	LOD = 7.2 ng/L
Berger 2004	SPE: Oasis HLB Plus cartridge	HPLC-TOF MS	NA	NA
Yamashita 2004, 2005, Taniyasu 2004a,b	SPE: Oasis HLB cartridge	HPLC-ES/MS/MS	LOQ = 0.8 pg/L	LOQ = 5.4 pg/L
Kannan 2004	SPE: Oasis HLB cartridge	HPLC-ES/MS/MS	LOQ > 2 ng/L	LOQ > 0.2 ng/L
So 2004	SPE: Oasis HLB cartridge	HPLC-MS/MS	LOQ = 5 pg/L	LOQ = 20 pg/L
Sinclair 2004, 2006	SPE: Oasis HLB cartridge	HPLC-MS/MS	LOQ = 0.8 ng/L	LOQ = 2.5-8 ng/L
Moody 1999	SPE: Strong Anion Exchange (SAX) disk	EI GC-MS	-	LOD = 18 μg/L LOQ = 36 μg/L
Skutlarek 2006	SPE: Phenomenx in Strata-x column	HPLC-MS/MS	LOD = 2 ng/L	LOD = 2 ng/L
Caliebe 2004	SPE: Chromabond HR-P resin	HPLC-ES/MS/MS	LOD = 0.05-0.5 ng/L	LOD = 0.05-0.5 ng/L
Moody 2001, 2002	-	^{19}F NMR	10 μg/L	-
Moody 2003	-	ES-MS	LOD = 3 μg/L LOQ = 5 μg/L	-

SPE is four-step process as shown in **Figure 3.1**. The SPE process provides samples that are in solution, free of interfering matrix components, and concentrated enough for detection. Steps include: (1) condition the SPE tube or disk, (2) add the sample , (3) wash the packing, (4) elute the compounds of interest. In reversed phase type silicas and nonpolar adsorption media usually are conditioned with a water-miscible organic solvent such as methanol, followed by water or an aqueous buffer. Methanol moistens surface of the sorbent and penetrates bonded alkyl phases, allowing water to wet the silica surface efficiently.

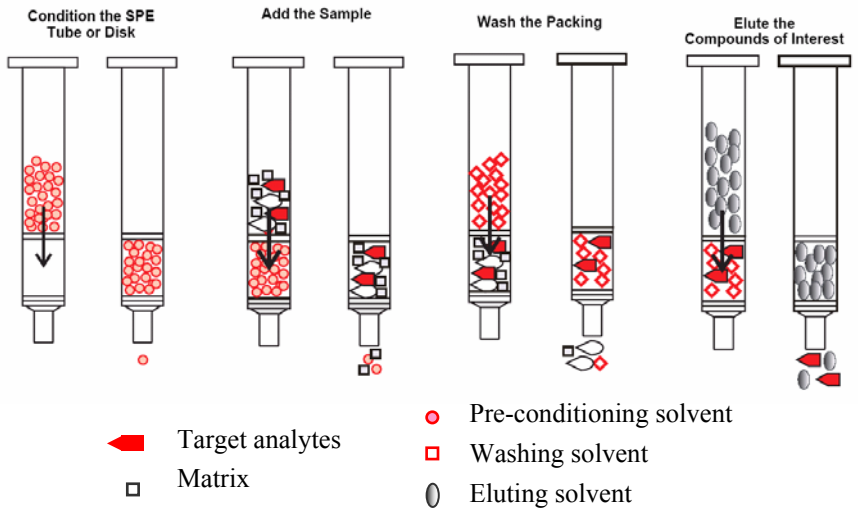


Figure 3.1 Steps in solid-phase extraction (SPE) for water concentrations

III.3 METHOD DEVELOPMENT FOR PFOS AND PFOA MEASURMENT IN SURFACE WATER

III.3.1 General sampling and analytical protocol

Glass and TEFLON materials were minimized during the whole sampling and analysis procedure because PFOS and PFOA may be binded to the glass in aqueous solution and TEFLON materials may introduce interferences.

For sampling, metal kettles and, some times, plastic bucket were used. They were rinsed with methanol followed by Milli-Q water to avoid cross contamination among different sampling. Disposable (polyethylene terephthalate) PET bottles having volume of 1L to 2 L were used as sampling bottles. After filtration, sample were transfer to polypropylene (PP) bottles. Samples after extraction were transferred in PP vial for LC/MS measurement.

In order to minimize the possibility of contaminants introduction, materials attached to sample were rinsed carefully with methanol and *Milli-Q* water before being used. They includes sampling bucket, sampling bottles, filter paper, filter system and vial, etc.

Considering that PFOS and PFOA are persistent, cooling samples might not be needed. However, to avoid other effects such as the growth of micro-organism, the formation of PFOS and PFOA from precursor substances or absorption of PFOS and PFOA on the solid

phase, cooling were normally preferred. Samples were preserved in the ice-cooling box during sampling and kept under 4^{o}C when arriving laboratory.

III.3.2 Standard and chemicals

PFOA acid (98% purity) and potassium salt of PFOS (95% purity) was used to make standard solution. Presep-C Agri cartridges (Solid phase: styrene divinylbenzene polymethacrylate) (Presep-C, 220 mg cartridge) and HPLC-grade methanol were used for sample extraction. All of the above chemicals and cartridges were purchased from Wako Pure Chemicals (Osaka, Japan).

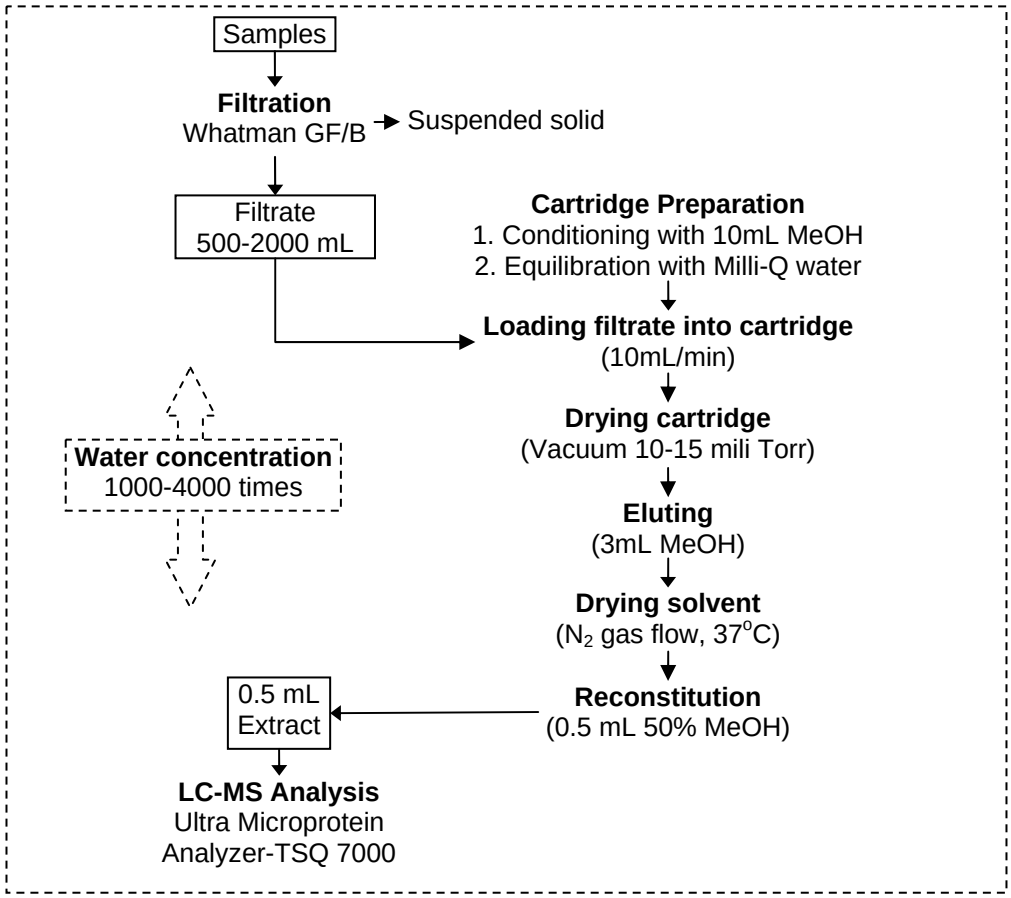


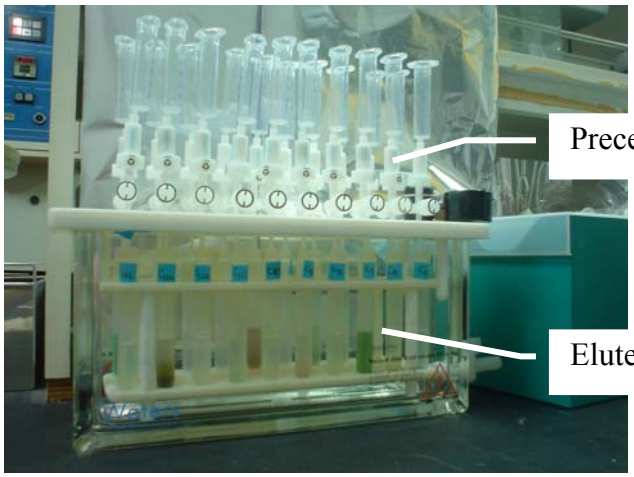
Figure 3.2 Analysis procedure

III.3.3 Analytical procedure

Determination of aqueous PFOS and PFOA concentrations was conducted by solid phase extraction (SPE) coupled with a high performance liquid chromatography tandem mass spectrometry (HPLC/MS).

III.3.3.1 Water concentration

A sample was firstly filtered through glass fiber filter (WHATMAN GF/B) to remove suspended solid. An appropriate volume (normally 1L or 2L) of the pre-filtered sample was loaded on Presep-C Agri cartridge at a flow rate of 10 mL/min using a concentration system (Sep-Pak® Concentrator Plus, Waters, Japan). The cartridge was then eluted with 3 mL methanol into a PP 10 mL tube and collected solvent in the tube was dried under N_2 gas flow at 37°C. The samples were reconstituted by adding a volume of 0.5 mL -1 mL HPLC solvent into the dried tubes and this is a final extract for LC-MS quantification.



III.3.3.2 HPLC-MS quantification

The HPLC/MS system used C-18 column and TSQ-7000 with optimized conditions shown in **Table 3.2.** Mobile phase included CH_3COONH_4 (A) and CH_3CN (B). It started with 55% B for first 2 min, followed by linear gradient application to increase B to 95% during next 7 min, and finally changed back to 55% B during last 0.5 min. The selected ion monitoring was applied at *m/z* values equal to 499 for PFOS anion ($C_8F_{17}SO_3^-$) and 413 for

PFOA anion ($C_7F_{15}CO_2^-$). PFOS and PFOA were detected at 6.0 min and 2.8 min respectively (**Figure 3.3**)

Table 3.2 LC-MS instrumentations and their optimized conditions for quantification of PFOS and PFOA

HPLC	
Instrument	Ultra Microprotein Analyzer
Column	Agilent Zorbax XDB C-18 (2.1x150 mm, 5mm)
Mobile phase	A: 10 mM CH_3COONH_4/H_2O; B: CH_3CN
Gradient application	1→ 2 min: A:B = 45:55 2→ 8 min: A: 45% → 5%; B: 55 → 95 8→ 8.5 min: A:B = 5:95 8.5 → 9 min: A: 5→ 45; B: 95 → 55 9 → 15 min: A:B = 45:55
Flow rate	0.2 mL/min
Oven temperature	30^{o}C
Injection volume	10 mL
MS	
Instrument	TSQ 7000 (ThremoQuest, USA)
Ionization	Electronspray ionization
Polarity mode	Negative
Sheath gas	N_2 (70 psi)
Auxilary gas	N_2 (10 mL/min)
Spray voltage	4200 V
Electron multiplier	1500 V
Capillary temperature	175^{o}C
SIM mode	PFOS: 499 (m/z); PFOA 413 (m/z)
Instrumental detection limits	0.3 pg
The limits of quantifications	PFOS: 0.05 ng/L (for concentration factor of 1000) PFOA: 0.1 ng/L (for concentration factor of 1000)

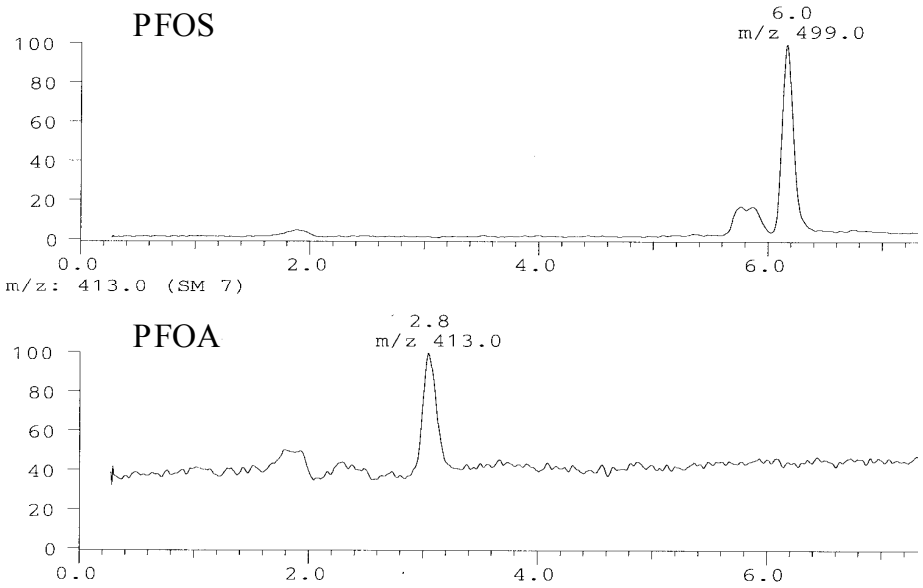


Figure 3.3 LC/MS chromatogram of PFOS and PFOA (blank sample spiked with 0.25 ng/L PFOS and 0.25 ng/L PFOA)

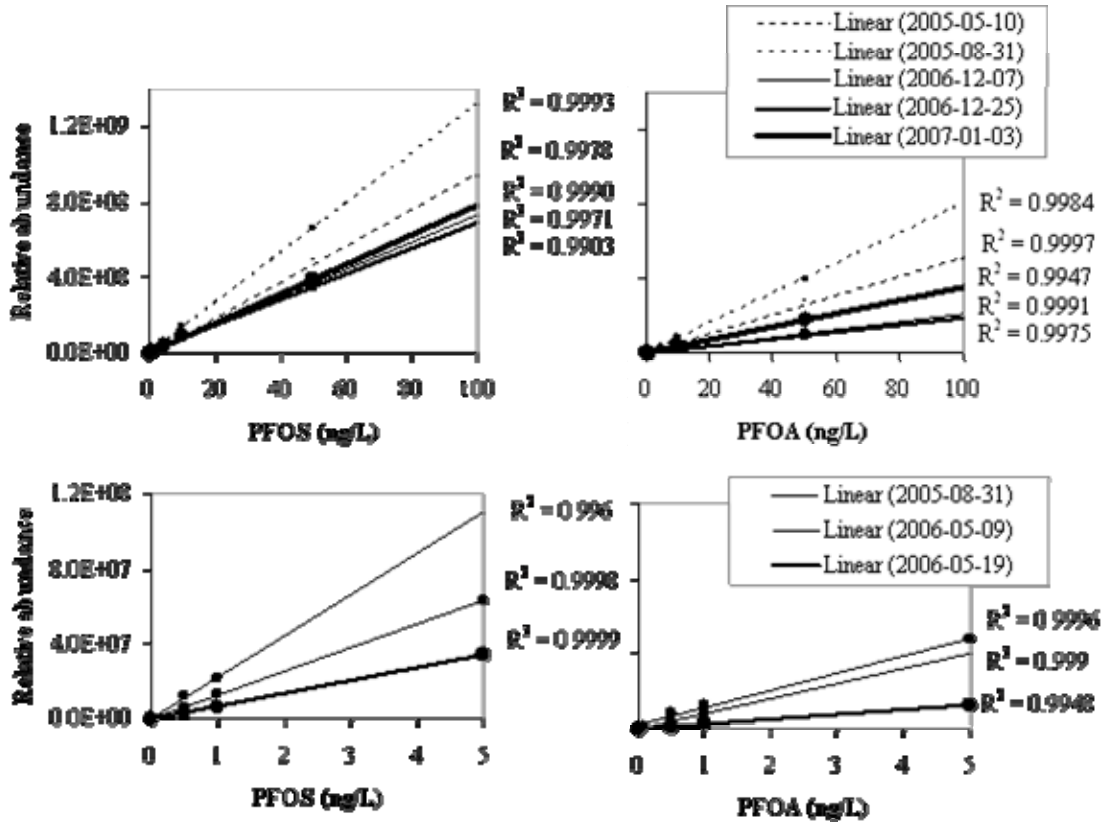


Figure 3.4 Standard curves on different days of analysis

III.3.3.3 Calibration curves and limits of detection

Limit of detection was set at signal-to-noise ratio of 3:1. Practically, the limit of quantification (LOQ) was used for detecting analytes. LOQ, which was defined by a coefficient of variation (CV) of less than 20%, was originally ranged from 0.05-0.1 µg/L for PFOS and 0.1-0.2 µg/L for PFOA, depending on day of operation. Actual LOQ was calculated based on the concentration factor, which resulted in 0.05-0.1 ng/L for PFOS and 0.1-0.2 ng/L for PFOA for the concentration factor of 1000 times.

III.3.4 Method validation

III.3.4.1 Extraction efficiency

Extraction efficiency experiment was conducted by spiking PFOS and PFOA in Milli_Q water at six different concentrations of 0.5, 1, 5, 10, 50 and 100 ng/L. These samples were prepared, concentrated and quantified according to the procedure mentioned above. They were calibrated against the calibration curved prepared in HPLC solvent. Extraction recovery of analytes in Mili-Q water ranged from 96%-109% for both PFOS and PFOA

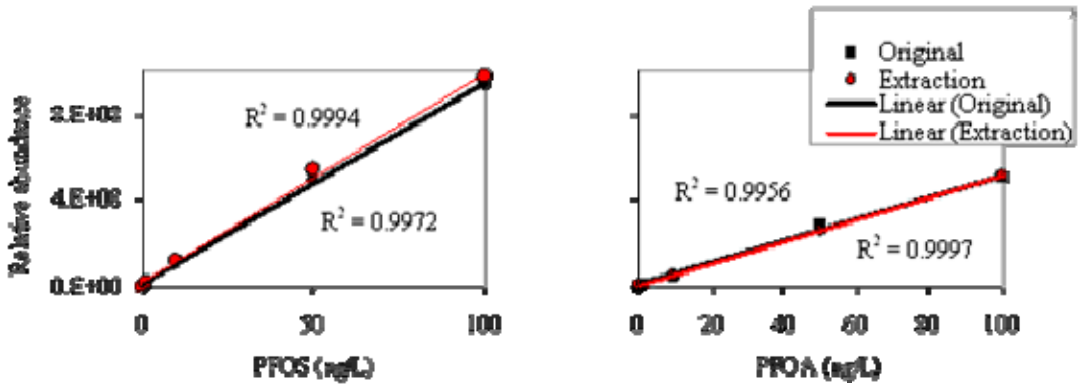


Figure 3.5 Original standard curves and extraction curves on a day of analysis

Table 3.3 Extraction recovery

Concentration	Recovery (%)	
(ng/L)	PFOS	PFOA
1	78	109
10	109	108
50	106	99
100	96	102

(**Table 3.3**). The extraction standard curves, for the concentration ranged from 0.5-100 ng/L for each analyte, were also linear with good determination coefficients (R^2 > 0.99) (**Figure 3.4**).

III.3.4.2 Recovery of environmental samples

Spiking of analytes into environmental samples was conducted in order to investigate the recovery. Tap water samples (a sample in Takatsuki, a sample in Kyoto), and surface water samples (a sample in Yamashina River, a sample in Kizu River, a sample in Yodo River) were spiked with 2, 5, 10, 1, 2 ng/L of PFOS and 40, 5, 50, 20, 10 ng/L of PFOA respectively. **Table 3.4** shows the recovery. The mean recovery was 87% and 95% for PFOS and PFOA respectively. In addition, for all systematic surveys, blank control measurement was conducted. Neither of PFOS or PFOA was detected in any of blank controls, which indicated that no contamination happened during sampling and pre-treatment.

Table 3.4 Recovery of environmental sample

	PFOS	PFOA
Number of samples	5	5
Field sample concentrations (ng/L)	0.8, 2.0, 2.8, 2.7, 5.9	6.7, 18.4, 28.3, 37.1, 42.6
Spiking concentration (ng/L)	1, 2, 2, 5, 10	5, 20, 20, 40, 50
Recovery (%)	87 ± 14	95 ± 20

III.4 SUMMARY

A qualified method for measurement of PFOS and PFOA in environmental water was developed. Analysis were conducted by SPE (solid phase extraction) coupled with HPLC-MS (high performance liquid chromatography tendem mass spectrometry). The method were able to quantified a minimum levels of 0.05-0.1 ng/L PFOS and 0.1-0.2 ng/L PFOA with water concentration factor of 1000 times. Standard curve for HPLC-MS were performed well with R^2 values above 0.99. Extraction recovery was within 10% different from expected values which is 100%.

CHAPTER IV

WATER SAMPLING SURVEYS

IV.1 INTRODUCTION

Water sampling survey is one of the major tasks of this research. This chapter is constructed to give an overview of sampling targets and sampling method. Main contents include (1) sampling campaigns for environmental water and tap water and (2) sampling and pre-treatment protocol. The content of this chapter, therefore, is a part of methodology part of the following three chapters.

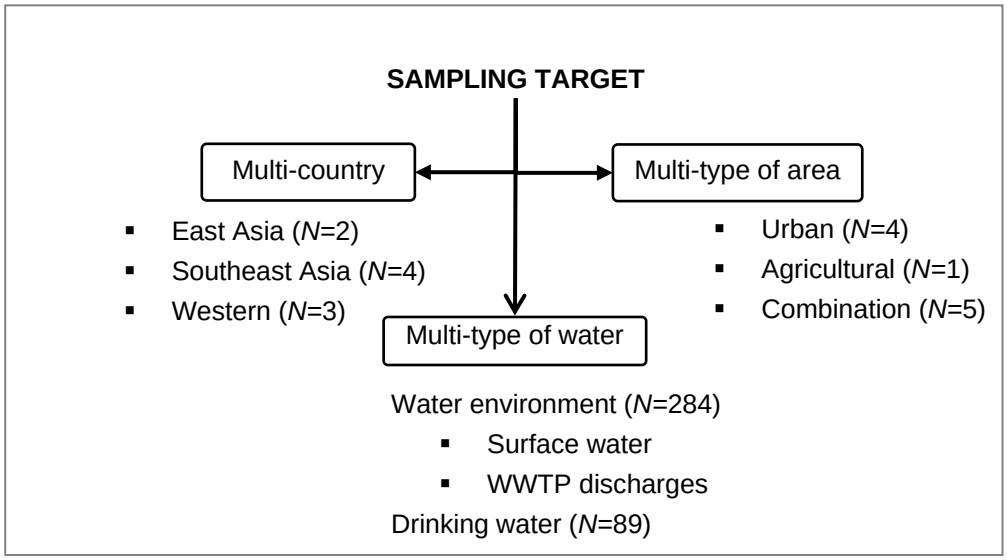


Figure 4.1 Sampling targets

A sketch of water sampling targets is shown in **Figure 4.1.** Sampling aims at various types of water: environmental water including surface water and wastewater treatment plant (WWTP discharge) as well as tap water. It target to collect these types of water from various countries: two countries in East Asia (Japan and China), four countries in Southeast Asia (Vietnam, Thailand, Malaysia, and Singapore) and three Western countries (Sweden, Turkey, and Canada). For each country, one or two areas were selected for

sampling so that targeted survey areas could be urbanized areas, agricultural areas or kinds of combination. In order to conduct surveys and collect water samples, sampling campaigns were planned and protocol for sampling method were set. They will be shown in the following

IV.2 SAMPLING CAMPAIGNS

Figure 4.2 shows a sketch of sampling campaigns. Samplings of all kinds of water were belong two schemes (1) systematic sampling surveys or (2) spot sample collection. Systematic surveys is the main scheme. In a systematic survey, sampling was planed to conducted for typical water throughout an area during a short periods (several days) while in spot sample collection scheme, spot samples were collected at random locations with no specification in time. Sampling locations which belong to these schemes are indicated in the Figure 4.2 and are illustrated in **Figure 4.3**.

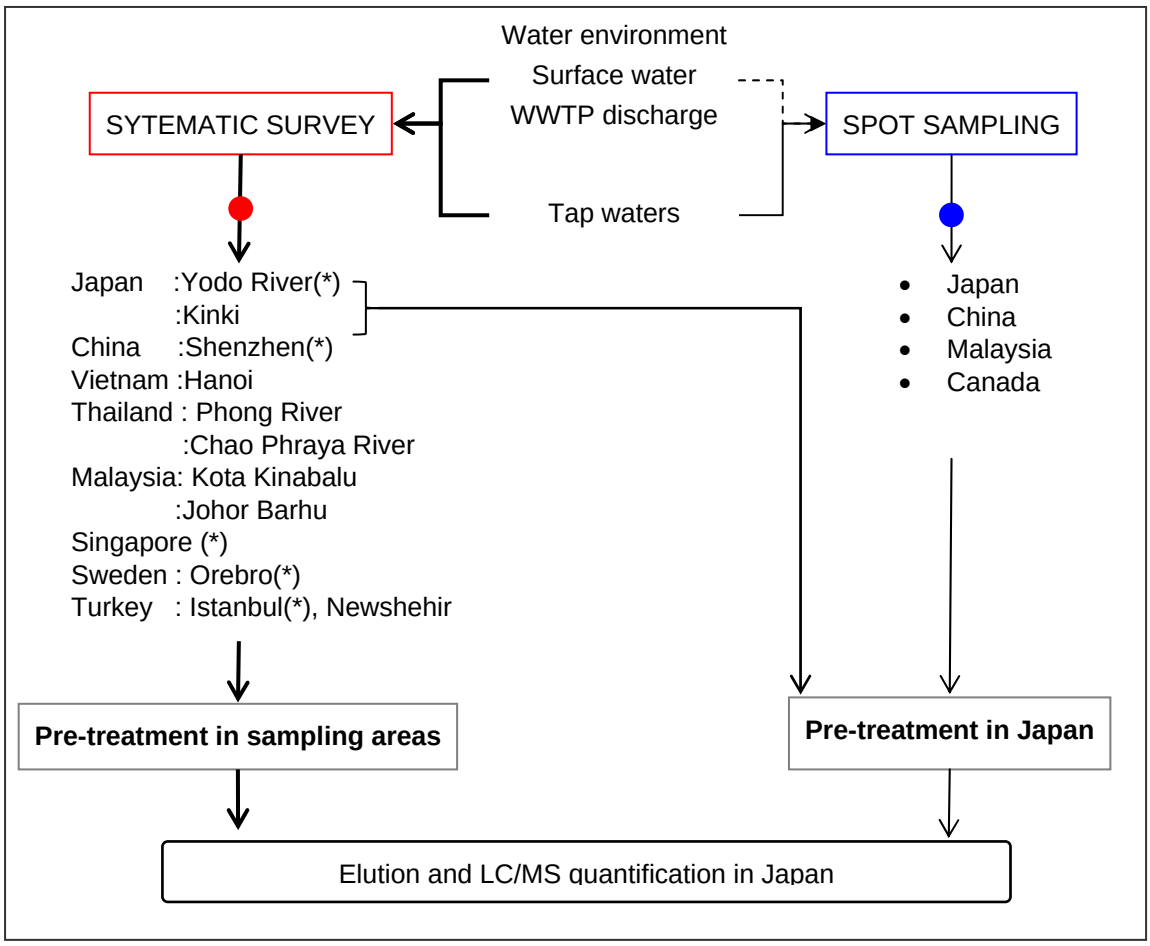


Figure 4.2 A sketch of sampling campaign

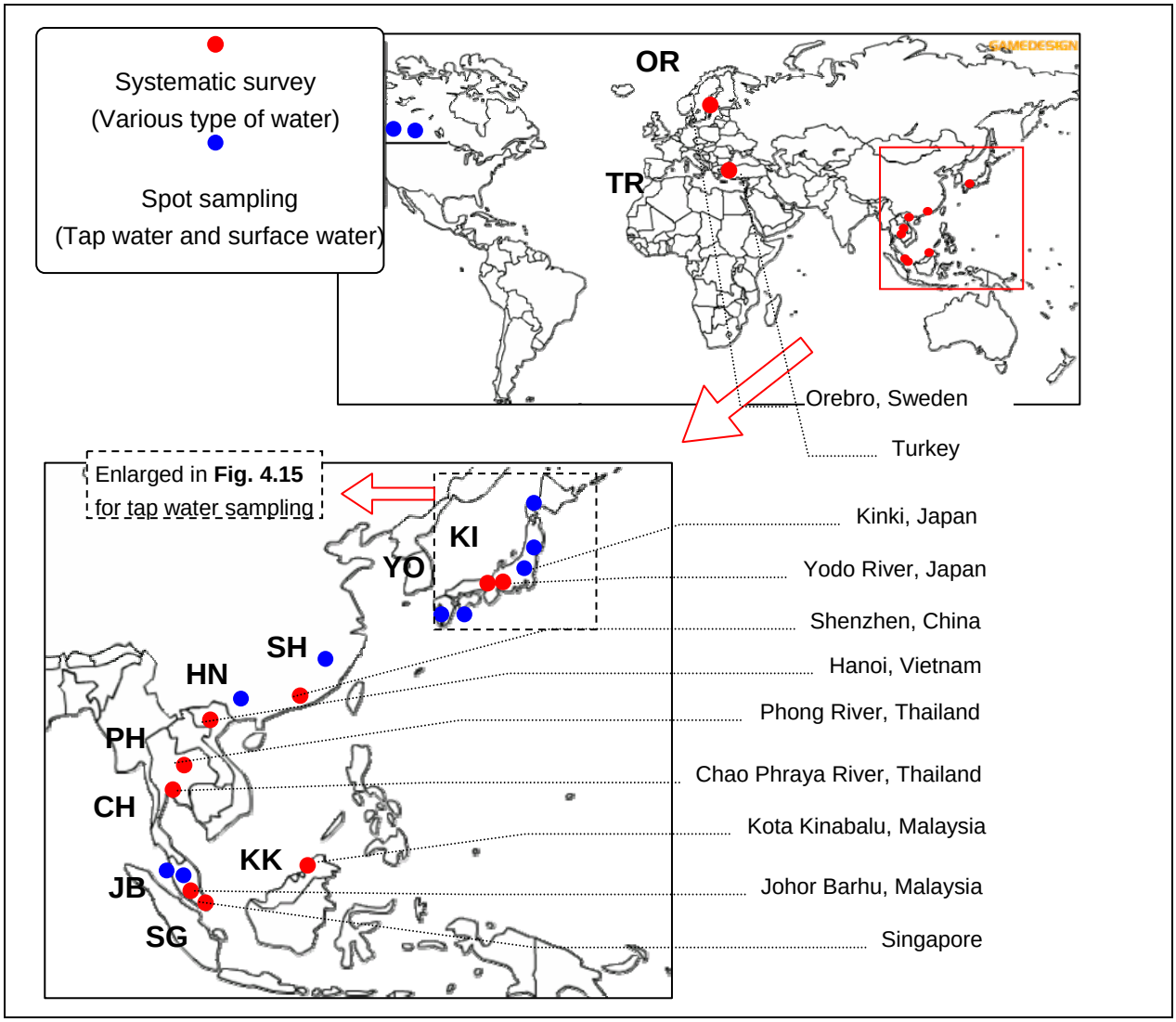


Figure 4.3 Locations of sampling areas for various type of water

IV.2.1 Systematic sampling survey for water environment

As shown in Figure 4.2, systematic survey areas included Yodo River (Japan), Kinki (when indicating Kinki, Yodo River which is located in Kinki areas is excluded) (Japan), Shenzhen (China), Hanoi (Vietnam), Phong River (Thailand), Chao Phraya River (Thailand), Kota Kinabalu (Malaysia), Johor Bahru (Malaysia), Singapore, Orebro (Sweden). Survey area's coordinate and approximate areas are shown in **Table 4.1** while their characterization in terms types, land areas, population are shown in **Table 4.2**. The table indicates that, sampling areas in this study were often within an urban area or extension of urban areas (combination) while one plainly agricultural areas were included.

Table 4.1 Locations of areas where systematic surveys were conducted

	Country	Area	Code	Range of latitude	Range of longitude	Approx. area (km x km)	Sampling type
1	Japan	Kinki	KI	33°26’- 35°4’1	134°18’ - 136°30’	160 x 170	Survey
2	China	Shenzhen	SH	22°27’ - 22°37’	113°52’ - 114°09’	15 x 25	Survey
3	Vietnam	Hanoi	HN	20°56’ - 21°07’	105°45’ - 105°54’	20 x 15	Survey
4	Thailand	Phong R.	PH	16°01’ - 17°40’	101°23’ - 103°12’	100 x 150	Survey
		Chao Phraya R.	CH	13°30’ - 14°45’	100°27’ - 100°37’	60 x 15	Survey
5	Singapore	Singapore	SG	01°15’ - 01°27’	103°37’ - 104°30’	20 x 40	Survey
6	Malaysia	Kota Kinabalu	KK	05°54’ - 06°07’	116°02’ - 116°13’	25 x 20	Survey
		Johor	JB	01°32’ - 01°38’	103°33’ - 103°44’	20 x 15	Survey
7	Sweden	Orebro	SE	59°15’ - 59°30’	14°54’ - 15°30’	30 x 35	Survey
8	Turkey	-	TR	-	-		Spot

Table 4.2 Characterization of survey areas and water sampling

	Name	Code	Type of samping area	Land area	Population	Population density (inh/km^2)
1	Yodo River	YO	Urban	8,240 (Catchment area)	11,000,000 (2007)	1,335
2	Kinki(*)	KI	Combination	7620 (Catchment area)	5,000,000 (2002)	656
3	Shenzhen	SH	Urban	465 (Urban)	8,000,000 (2005)	17,200
4	Hanoi	HN	Urban	921 (Urban)	3,145,300 (2005)	3,348
5	Phong River	PH	Rural	15,059 (Catchment area)	1,617,000 (2005)	107
6	Chao Phraya River	CH	Combination	21,521 (Catchment area)	11,500,000 (2002)	533
7	Kota Kinabalu	KK	Combination	351 (City)	532,129 (2007)	1,516
8	Johor Bahru	JB	Combination	1,871 (District)	1,278,000 (2001)	703
9	Singapore	SG	Urban	704 (Country)	4,483,900 (2006)	6,369
10	Orebro	OR	Combination	1,380 (Municipality)	128,977 (2006)	93

*Note: *** Kinki indicates Kinki excluding Yodo River system while sampling*

There were also differences in terms of population density ranging from 93 inhabitate/km^2 in Orebro to 6,369 inhabitate/km^2 in Singapore. Surface water sampling in the areas, depend on geological property, could be river system water or general (various kind of surface water). Description of survey area and sampling map will be shown in detail.

IV.2.1.1 Description of sampling areas and water surveys

(1) ***Yodo River system (Japan)***

The Yodo River system runs through the Kinki region of Japan where over 13 millions people lives (**Figure 4.4)** and is one of the most important River in Japan**.** It has a catchment area of approximately 8,240 km^2. Most wastewater is discharged in the upper river basin, while most drinking water is abstracted downstream.

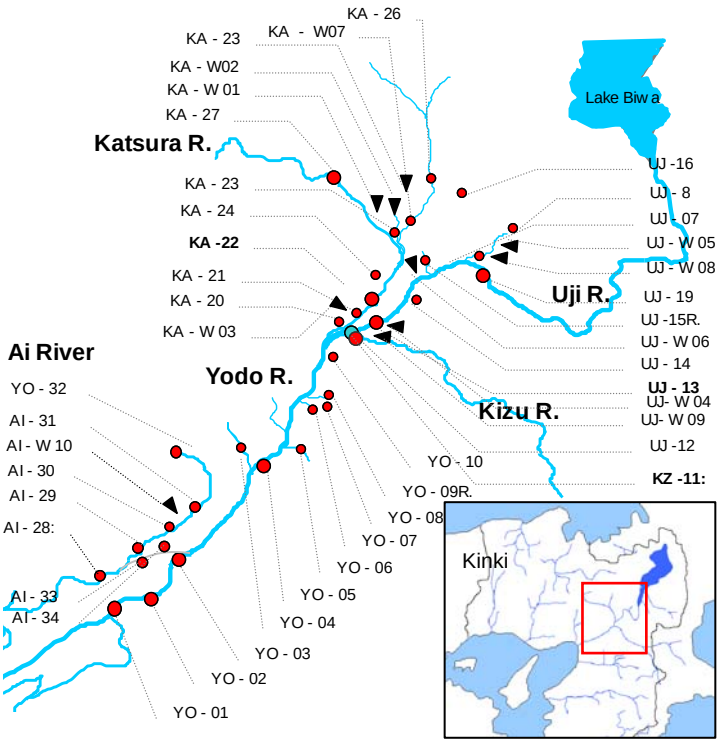


Figure 4.4 Sampling locations in Yodo River

Three surveys were conducted in the mid and lower basins of Yodo River including Ai River which run in parallel with Yodo River. Water sample collected are of two kinds (1) surface water in mainstreams and tributaries and (2) wastewater treatment plant (WWTP) discharges The number of sampling locations for surface water is 34 in total, including 8 in Katsura sub-basin, 8 in Uji sub-basin and, 1 in Kizu River, 10 in Yodo River downstream sub-basin and 7 in Ai River sub-basin. Kinki Region - KI (Japan). Sampling locations are shown in **Figure 4.4**.

(2) ***Kinki (Japan)***

Kinki is an region of Japan where Yodo River system located. Sampling are extended in Kinki Region that beyond Yodo River system. Kinki region cover a land area of 31,517 km^2, in which 9,527 km^2 is habitable land (8.3% of Japan). Its population of 21,865 thousands accounts for 17% of Japanese populattion. Sampling surveys were conducted in the main river system except for Yodo River system in Dec-06. Water samples were collected in Kino River (1 location), Yamato River (2 locations), Ina River (2 locations), Kako River (4 locations), Ichi River (2 locations), Ibo River (1 locations) and Yura River (3 locations). Sampling locations are shown in **Figure 4.5**.

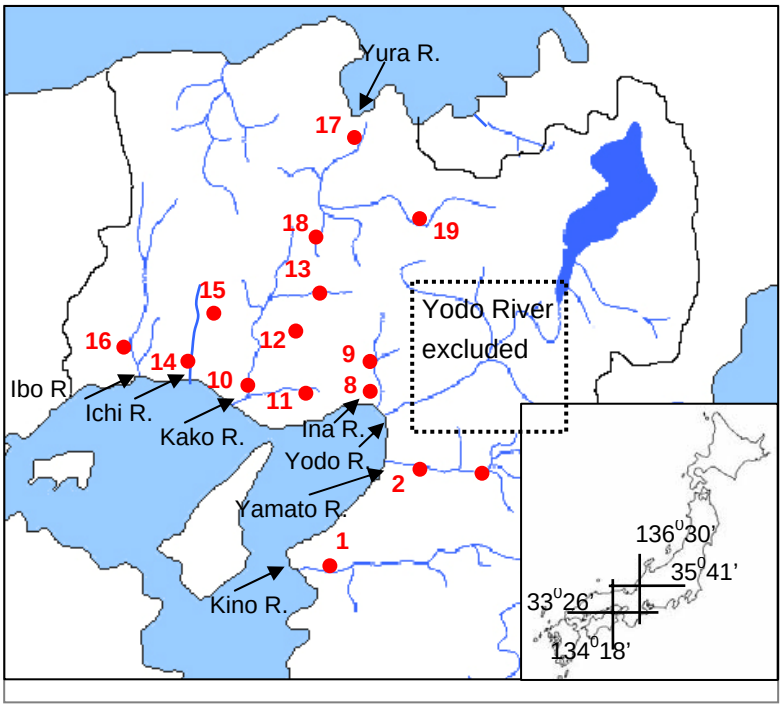


Figure 4.5 Sampling locations in Kinki Region (Japan)

(3) ***Shenzhen (China-SH)***

Shenzhen, a sub provincial city of Guangdong province in southern China is selected as an samping survey area in China. It has been the fastest growing city in China for the past thirty years and is likely to be the most rapidly evolving city in the world. Sampling survey was conducted in Oct-2006. Water samples were taken from rivers passing through Futian district and Nanshan district (8 locations), coastal water in Shenzhen Bay (1 location), and 2 water

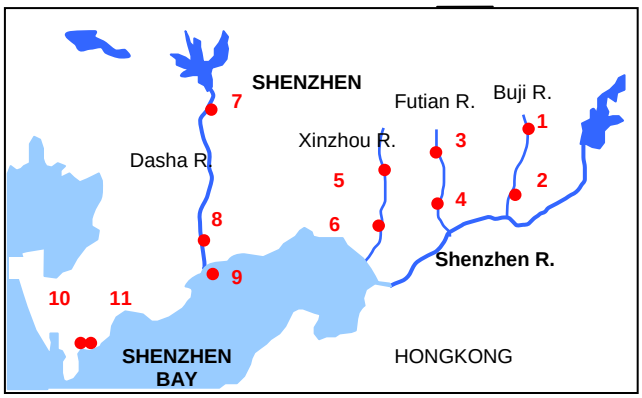


Figure 4.6 Sampling locations in Shenzhen

samples from wastewater treatment plant located in Nanshan. Sampling locations are shown in **Figure 4.6.**

(4) ***Hanoi (Vietnam-HN)***

An area selected for sampling survey in Vietnam is Hanoi city, the capital of Vietnam. Hanoi is a major metropolitan area of Northern part and it is located in the right bank of Red River, a River starting from China. Water samples were collected from rivers passing through the city (5 locations), drainage canals (4 locations), and lakes (3 locations) in Jan-06. Sampling locations are shown in **Figure 4.7**

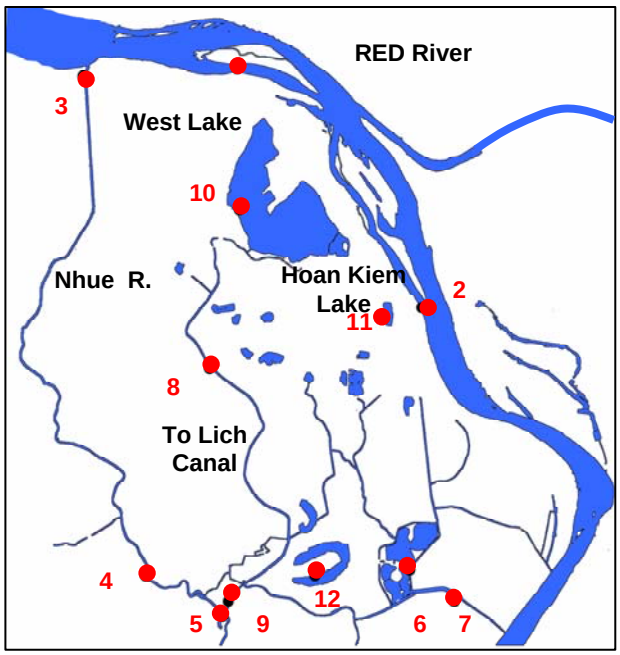


Figure 4.7 Sampling locations in Hanoi

(5) ***Phong River basin - PH (Thailand)***

The first area of samping survey in Thailand is Phong River basin. The Phong River basin is located in the northeast part of Thailand covering an area of approximately 15 thousand km^2 (Songprasert 2005). The basin, which is a part of Mekong River basin that is the most important basin in Southeast Asia, is characterized as an agricultural area. Four main streams flow in the upstream

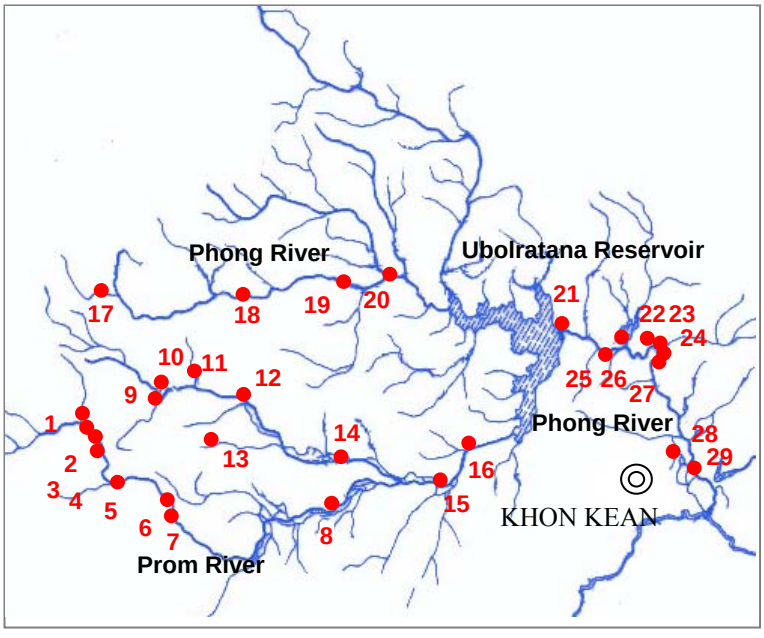


Figure 4.8 Sampling locations in Phong River

sub-basin toward the Ubolratana Reservoir where is the biggest water body in the watershed. Sampling surveys were conducted twice, in Jul-05 and in Jan-06. Samples were collected at 29 locations which included 8 locations in Prom R.; 8 locations in Choen R.; 4 locations in Phong R. upstream, and 9 locations in Prong R. downstream. Sampling locations are shown in **Figure 4.8**.

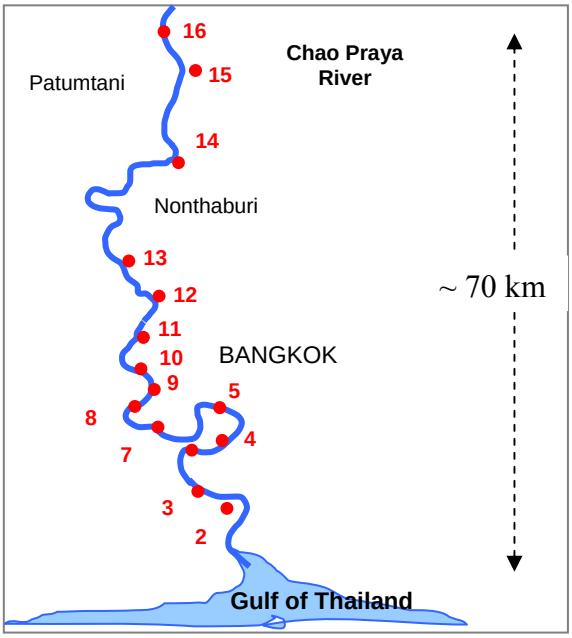


Figure 4.9 Sampling locations in Chao Praya River

(6) ***Chao Phraya River - CH (Thailand)***

The second sampling survey in Thailand is Chao Phraya River. Chao Phraya River is the most important River in Thailand. The River's basin cover 30% of country area, is home to some 40% of country population. The basin can be divided into eight sub-basins and ended with Chao Phraya sub-basin where sampling where conducted. Chao Phraya basin has catchment area of 21,000 km^2 and is home of about 50% of basin population (11.5 million), in which the highly populated areas of Bangkok Metropolitan Area are located. Chao Phraya River is 375 km long, and water samples were collected along 100 km downstream, at 15 locations. Sampling locations are shown in **Figure 4.9**.

(7) ***Kota Kinabalu - KK (Malaysia)***

The first area selected for sampling survey in Malaysia is Kota Kinabalu City - one of the

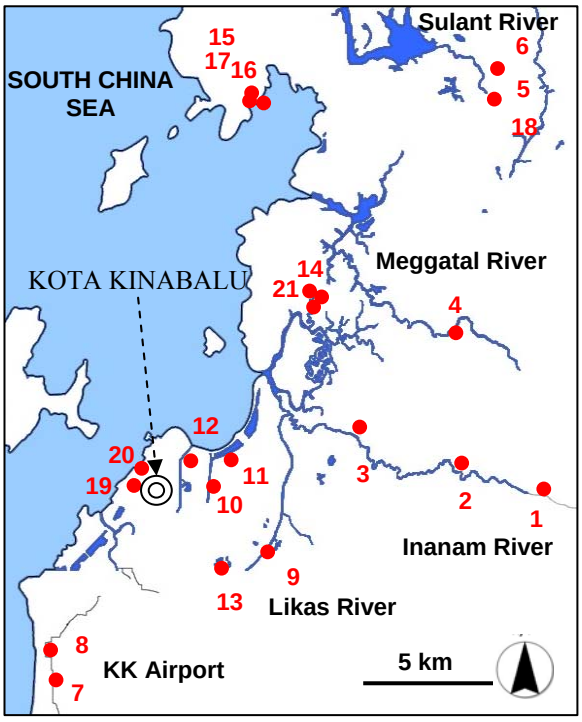


Figure 4.10 Sampling locations in KK

major industrial and commercial centers in East Malaysia. The city is a coastal city in Borneo Island, lying on a narrow flatland and itself contains several hills which are mostly covered with tropical rainforest. Water samples were collected from river (9 locations); lake, pond and wetland (8 locations); drainage (2 locations), and plash (2 locations). Sampling locations are shown in **Figure 4.10**. Sampling surveys were conducted in two periods (Aug-2005 and Nov-05) in which in some of locations, sampling was repeated.

(8) ***Johor Bahru - JB (Malaysia)***

The second survey area in Malaysia is the Johor Bahru, West Malaysia. Johor Bahru city is an important industrial and commercial centre for southern Malaysia. It is also one of Southeast Asia's most populous urban areas. Metropolitan Johor Bahru occupies extensive coastal land consisting of ecologically rich swamp lands and important river systems such as Sungai Johor, Sungai Pulai and Sungai Tebrau. Water samples were taken from two rivers Sungai Tebrau (3 locations) and Sungai Skudai (3 locations) in Oct-06. Sampling locations are shown in **Figure 4.11**.

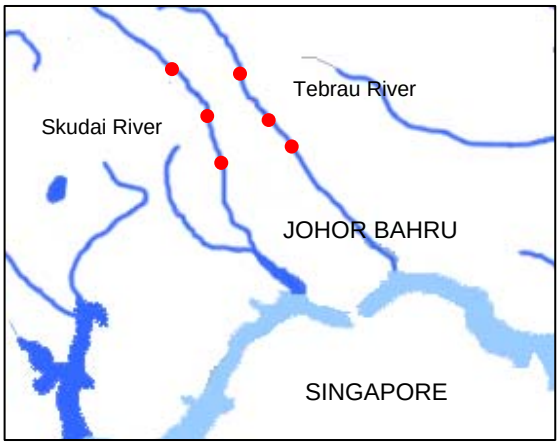


Figure 4.11 Sampling locations in Johor Bahru (Malaysia)

(9) ***Singapore – SG***

Located just below Johor Bahru, Malaysia, Singapore Island is the smallest country in Southeast Asia with an area of 704 km². The country is nearly entirely built-up and urbanized. It has no natural freshwater rivers and lakes, but domestic fresh water is created by collecting rainfall in reservoirs or catchment areas. A sampling survey was conducted in Singapore in Oct-2006 on various type of water. Samples were collected from reservoirs (9 locations), non-catchment streams (11 locations), coastal sea (4 locations) and discharges from wastewater treatment from wastewater treatment plant in the country (10 locations). Sampling locations are shown in **Figure 4.12**.

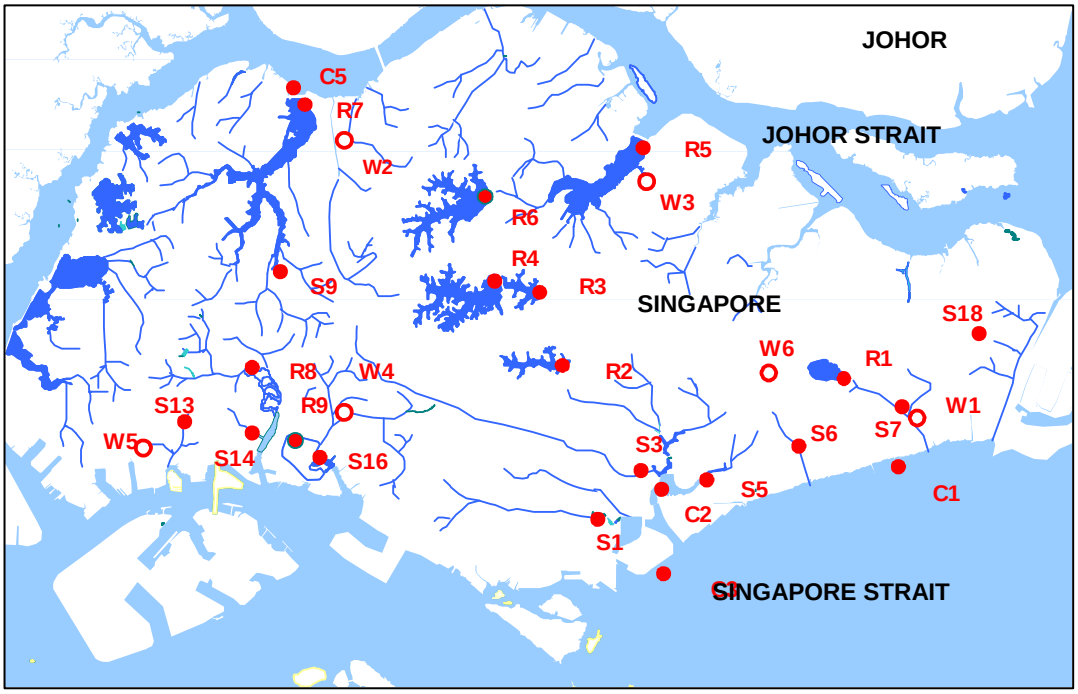


Figure 4.12 Sampling locations in Singapore

(10) ***Örebro - SE (Sweden)***

Örebro Municipality is a municipality in central Sweden where the Örebro is the seat of government. At a population density of 93 inhabitant/km^2 in an area of 1,380 km², it is the less populated area in this study. Sampling survey were conducted on various kinds of water in the main towns including Orebro City in Mar-05. Water samples were taken from rivers (6 locations), lakes (5 locations), wastewater treatment plant discharges (4 locations) and a snow samples from a ski center. Sampling locations are shown in **Figure 4.13**.

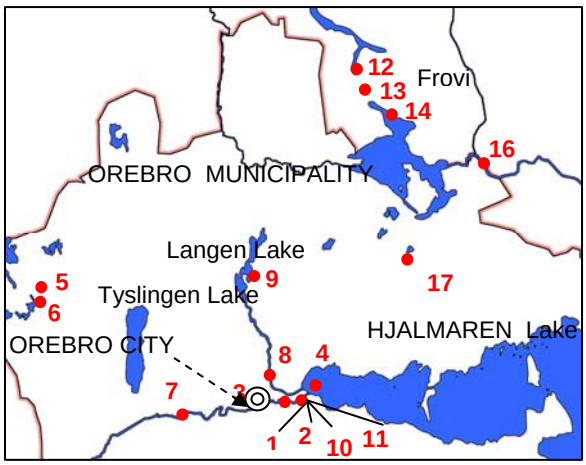


Figure 4.13 Sampling locations in Orebro

(11) ***Turkey - TR***

Spot sampling was conducted in Turkey with a total samples number of five. Lake water samples were collected in 2 locations in Terkos Lake and Sazlidere Lake. River water samples were collected in 2 locations including one locations in Red River (Kızıl River), the longest River in Turkey. One wastewater sample was collected in Istanbul. Sampling locations are shown in **Figure 4.14.**

Figure 4.14 Sampling locations in Turkey

IV.2.1.2 Summary of water surveys

Table 4.3 Number of sampling locations and collected samples

Area	**Collected sample**	Sampling locations				
		Total Site	River	Dam, Reservoir, Lake, Pond, Wetland	Other surface water	WWTP water
Yodo R. (YO)	**94**	**48**	35	3	-	10
Kinki (KI)	**15**	**15**	10	5	-	-
Shenzhen (SH)	**11**	**11**	8	-	1	2
Hanoi (HN)	**12**	**12**	6	3	3	-
Phong R. (PH)	**46**	**29**	21	8	-	-
Chao Phraya R. (CH)	**15**	**15**	15	-	-	-
Singapore (SG)	**34**	**34**	11	9	4	10
Kota Kinabalu (KK)	**30**	**21**	10	7	4	-
Johor (JB)	**6**	**6**	6	-	-	-
Turkey (TR)	**5**	**5**	2	2	-	1
Orebro (OR)	**16**	**16**	6	5	1	4
Total	**284**	**212**	**130**	**42**	**13**	**27**

Overall, samples were collected at 212 locations in total, in which there are 185 locations of surface water and 27 of WWTP discharges. **Table 4.3** shows a summary of sampling which indicates number of sampling locations in each area and for each type of water. Sampling time is within November 2004 and December 2006. Sampling times are summarized in **Table 4.4** that also indicates that single collection were conducted for

majority of sampling areas while repeated sampling were conducted in Phong River and Kota Kinabalu as examples to confirm contamination levels.

Table 4.4 Sampling periods for systematic surveys

Sampling area	2004	2005				2006					
	Nov	Mar	Jul	Aug	Nov	Jan	Mar	Sep	Oct	Nov	Dec
Yodo R. (YO)	25th	16th			1st						
Kinki (KI)											19- 27th
Shenzhen (SH)									19-20th		
Hanoi (HN)						23-28th					
Phong R. (PH)			14-17th			16-19th					
Chao Praya R. (CH)											6th
Kota Kinabalu (KK)				29-9thSep	2nd						
Johor (JB)									9th		
Singapore (SG)									2-7th		
Orebro (OR)							7-8th				
Turkey (TR)								18-22th			

IV.2.2 Tap water collection

Sampling of tap water were conducted by two schemes: collection of tap water in the same environmental water survey areas and spot collection of for other locations.

IV.2.2.1 Sampling in environmental water surveys areas

Firstly, tap water samples were collected from locations within areas that have surface water survey described above. Because one of the objectives is to find out similarity between tap water and surface water concentration. Tap water samples were collected in Shenzhen (*N*=5)), Hanoi (*N*=2), Khon Kaen in Phong River basin (*N*=3), Bangkok and other cities in Chao Phraya River basin (*N*=7), Johor Bahru (*N*=2), Kota Kinabalu (*N*=4), Istanbul (*N*=4), Orebro (*N*=2). Collection of tap water often conducted at the same period with surface water surveys. Repeated sampling were conducted in several areas.

IV.2.2.2 Spot sampling in other locations

Tap water samples were collected from the location beyond surface water sampling areas, in several countries. Collection of tap water were more intensively in Japan and sampling locations are shown in **Figure 4.14**. Other sampling locations includes Hangzhou (*N*=1)

and Kunming (*N*=1) in China, Penang (*N*=1) and Kuala Lumpur (*N*=2) in Malaysia, Vancover (*N*=1) and Calgary (*N*=1) in Canada. In addition, spot samples of surface water were also taken from Hangzhou (*N*=1) and Vancouver (*N*=1).

IV.2.2.3 Survey of tap water in Kinki (Japan)

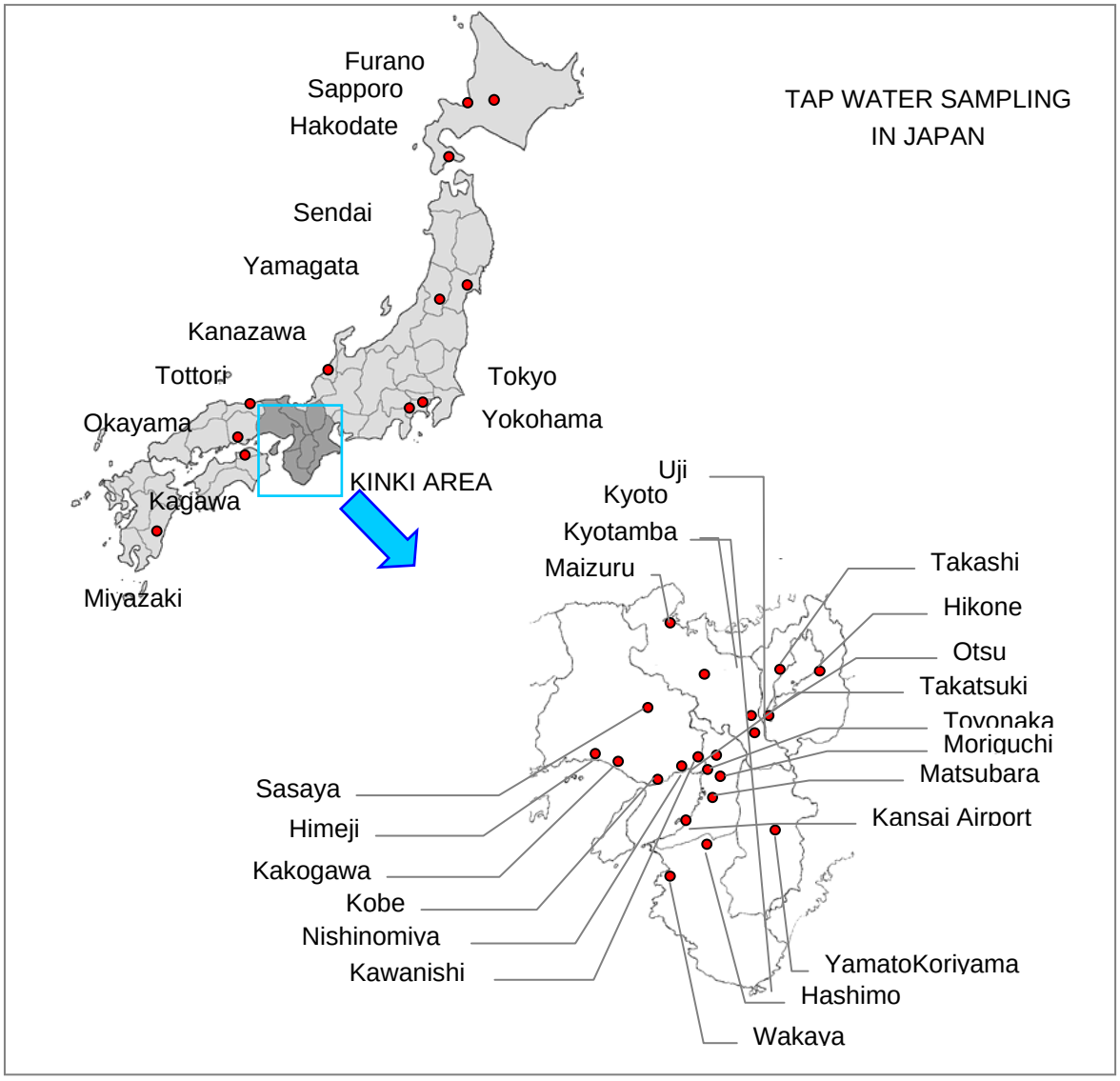


Figure 4.15 Tap water sampling locations in Japan

A systematic survey of tap water were conducted in Kinki Area (*N*=36). Sampling locations were shown in **Figure 4.15**. Samples was collected from main cities of six prefectures. Because one of the objective is to find out the relation between tap water and its water sources, sampling were also focused on location have sources from different river

system in the region. The number of sampling location in Kinki are within 4 cities in Kyoto prefecture, 3 cities in Shiga prefecture, 6 cities in Kobe, 5 cities in Osaka, 2 cities in Wakayama, and 1 cities in Nara. Some of sampling locations have repeated sampling in order to confirm concentration levels. Identification of water sources will be shown in **Chapter VII**.

IV.2.2.4 Summary of tap water collection

A summary of tap water collection are shown in **Table 4.5**. Totally 89 tap water samples were collected and the majority are collected in environmental water survey areas. The table indicates corresponding areas where surface water surveys were conducted.

Table 4.5 A summary of tap water sampling locations and number of samples

Country	Tap water		Corresponding surface water	
	Sampling area	Sample number	Sampling area	Note
Japan	Kinki	**36**	Kinki	
	Others	**16**	-	Not available
China	Shenzhen	**5**	Shenzhen	
	Hangzhou	**1**	Hangzhou	Spot sampling
	Kunming	**1**	Kunming	Spot sampling
Vietnam	Hanoi	**2**	Hanoi	
Thailand	Bangkok,	**7**	Chao Praya River	
	Khon Kaen	**3**	Phong River	
Malaysia	Kota Kinabalu	**4**	Kota Kinabalu	
	Johor Bahru	**2**	Johor Bahru	
	Penang, Kuala Lumpur	**3**	-	Not available
Turkey	Istanbul	**4**	Istanbul	Spot sampling
	Newsehir	**1**	Newsehri	Spot sampling
Sweden	Orebro	**2**	Orebro	
Canada	Vancover	**1**	Vancover	Spot sampling
	Calgary	**1**	-	Not available
Total		**89**		

IV.3 PROTOCOL FOR SAMPLING AND PRE-TREATMENT OF SAMPLES COLLECTED OUTSIDE JAPAN

IV.3.1 Sampling protocol

Glass and TEFLON materials were minimized during the whole sampling and analysis procedure because PFOS and PFOA may bind to the glass in aqueous solution and TEFLON materials may introduce interferences.

For sampling of environmental water, metal kettles and, some times, plastic bucket were used. They were rinsed with methanol and Milli-Q water to avoid cross contamination among different sampling. Disposable (polyethylene terephthalate) PET bottles having volume of 1L to 2 L were used as sampling bottles. After filtration, sample were transfer to polypropylene (PP) bottles. Samples after extraction were transferred in PP vial for LC/MS measurement.

Sampling of tap water was conducted by direct collection from tap of either public place or household. PET bottle (typical volume of 2L were used for sampling). Tap water sample collected in environmental surveys areas are handle in similar way with environmental samples. Spot samples were brought back our laboratory without any pre-treatment basically within a couple of days. Cooling of samples was not needed in the protocol.

In order to minimize the possibility of contaminants introduction, materials attached to sample were rinsed carefully with methanol and *Milli-Q* water before being used. They includes sampling bucket, sampling bottles, filter paper, filter system and vial, etc.

Considering that PFOS and PFOA are persistent, cooling samples might not be needed. However, to avoid other effects such as the growth of micro-organism, the formation of PFOS and PFOA from precursor substances or absorption of PFOS and PFOA on the solid phase, cooling were normally preferred. Samples were preserved in the ice-cooling box during sampling and kept under 4^{o}C when arriving laboratory.

IV.3.2 Pre-treatment protocol

As shown in Figure 4.2, while samples collected in Japan and spot samples were preserved and transported to laboratory within the day of sampling for analysis, samples collected outside Japan in systematic survey were pre-treated before transported to Japan. The principle of pre-treatment was consistent for all collected samples in Japan and outside Japan but places of conducting was different.

Figure 4.16 shows a simple protocol to handle samples collected in systematic surveys outside Japan. It shows pre-treatment steps to be conducted in sampling country and following step to be conducted in Japan. In short, samples was loaded into Presep-C Agri

cartridge in survey countries. In order to conduct this, a set of sampling equipment were prepared to conduct pre-treament. They include materials such as filters, cartridges and a concentration system for water concentration. This was conducted in Partner Universities as shown in **Table 4.6** where chemicals needed were supported.

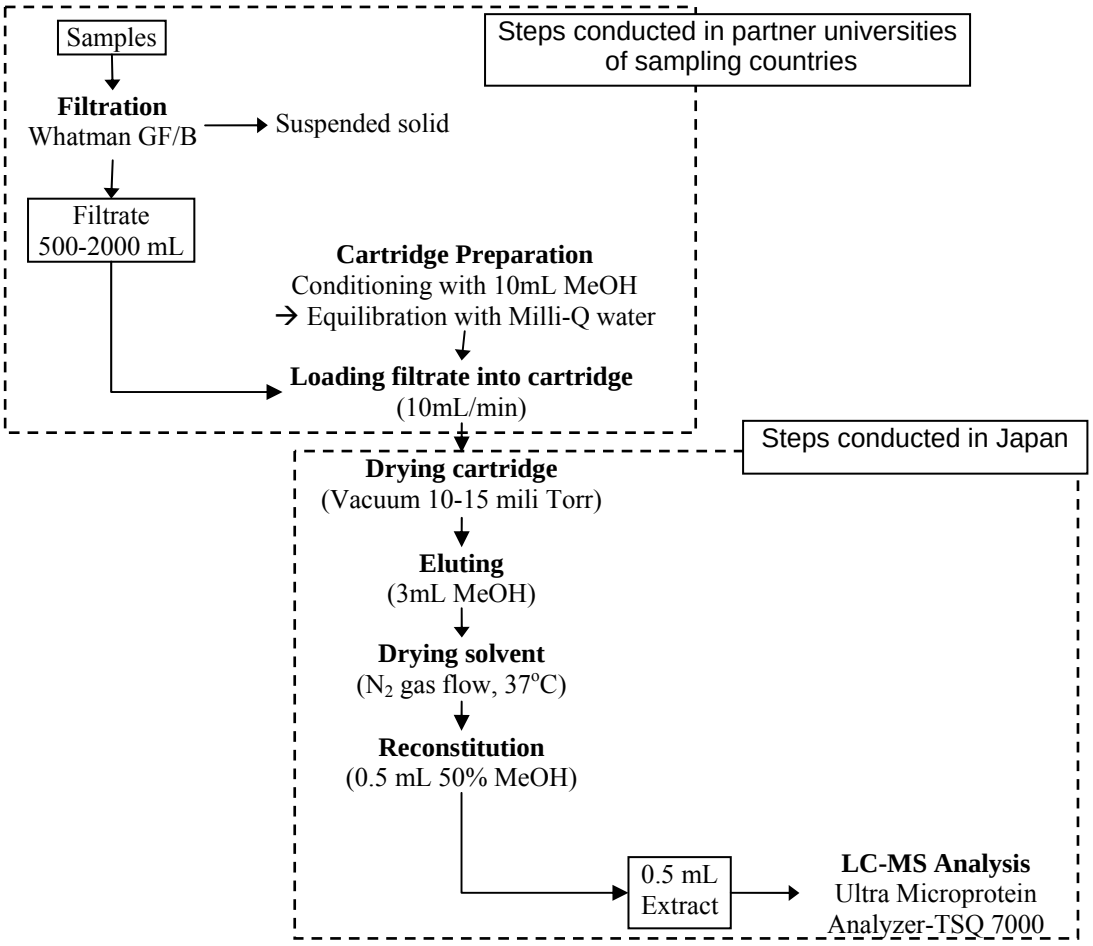


Figure 4.16 A simple procedure for pre-treatment and analysis of PFOS and PFOA from various locations

By this way, samples were partly pre-treated and reserved before transportation to Japan. Sample-loaded cartridges were kept cool at about 4°C during transportation to Japan for remaining extraction steps and LC/MS analysis.

Table 4.6 List of partner universities where sample pretreatment was conducted

Country	Sampling area	Partner University	Pure water	Methanol
China	Shenzhen	Tsinghua University in Shenzhen	Milli_Q	high-grade
Thailand	Phong R.	Khon Kean University	Milli_Q	high-grade
	Chao Praya R.	Mahidol University	DI	high-grade
Vietnam	Hanoi	Hanoi University of Technology	Milli_Q	high-grade
Malaysia	Kota Kinabalu	University Malaysia Sabah	Milli_Q	high-grade
	Johor	University Technology Malaysia	Milli_Q	high-grade
Singapore	Singapore	National University of Singapore	Milli_Q	high-grade
Sweden	Orebro	Orebro University	Milli_Q	high-grade
Turkey	Istanbul	Istanbul Technical University	DI	high-grade

IV.4 SUMMARY

This chapter explained water sampling surveys and sample collection for environmental water and tap water.

1) Sampling campaign was described indicating that environmental water survey and tap water collection were conducted in eight countries. Overall, two schemes of sampling were applied to collected samples those are: systematic survey and spot sample collection. While most of environmental water were systematically collected by systematic survey, tap water were also collected by spot sampling schemes.

Environmental water survey areas were described. Sampling period and type of water samples together with sampling locations were identified.

Tap water water collection were conducted by several ways. Firstly, tap water were collected in environmental water survey areas. Secondly, spot sample of tap water collection in other indicated locations. Finally, a survey of tap water in Kinki Japan were described.

2) Sampling method and pre-treatment protocol was described. A set of pre-treatment equipment were prepared to pre-treat sample collected outside Japan so that samples were partly pre-treated and preserved before transportation to Japan for further analysis. Sample were pre-treated by extraction of PFOS and PFOA into cartridge. This was conducted in

partner university with support of chemical needed. Following analysis has been described in Chapter III.

In the following chapters, environmental water (surface water and WWTP discharge) and tap water result will be shown and discussed separately

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CHAPTER V

PFOS AND PFOA POLLUTION IN WATER ENVIRONMENT

V.1 INTRODUCTION

Water is the most concerned non-biota environment for PFOS and PFOA. However, reported data on PFOS and PFOA concentrations were far less in order to understand their distribution in environmental water, especially inland surface water. Data have been increasing recently but reported areas in literature were limited in USA, Japan and EU countries (Hansen *et al.* 2002, Saito *et al.* 2004, Sinclair *et al.* 2004, 2005, Berger *et al.* 2004). It was indicated trace levels of PFOS and PFOA at low ng/L or µg/L levels in environmental water. There were possible link between contamination with production and use of these compounds in those countries.

Production and application of PFOS, PFOA and their related chemicals seem to be worldwide (**Chapter II**). Therefore, it is expected their contamination in many parts of the world. For example, there is production of perfluorinated compounds in China and in Malaysia, but contamination of PFOS and PFOA in surface water have not been examined. Because of the fact that PFOS, PFOA and its precursors are involved in various commercial products and that they possibly have POPs characteristics, there is a strong need to know their distribution in global scale.

With an attempt to recognize the distribution of PFOS and PFOA in new places, this chapter aims at determination of PFOS and PFOA concentrations in samples collected from surface water and WWTPs discharges of various areas with focus on places where examination of PFOS and PFOA in water have not been conducted. A sketch of sampling plan and expected outcomes are shown in **Figure 5.1**. Results and discussion will be shown in four parts: (1) surface water concentrations in individual sampling areas and reproducibility of concentrations (2) spatial variation in concentration levels (3) concentration in WWTP discharges versus surface water (4) Effects of PFOS and PFOA

contamination on ecosystems (5) PFOS and PFOA relationship, relationship of PFOS and PFOA with DOC.

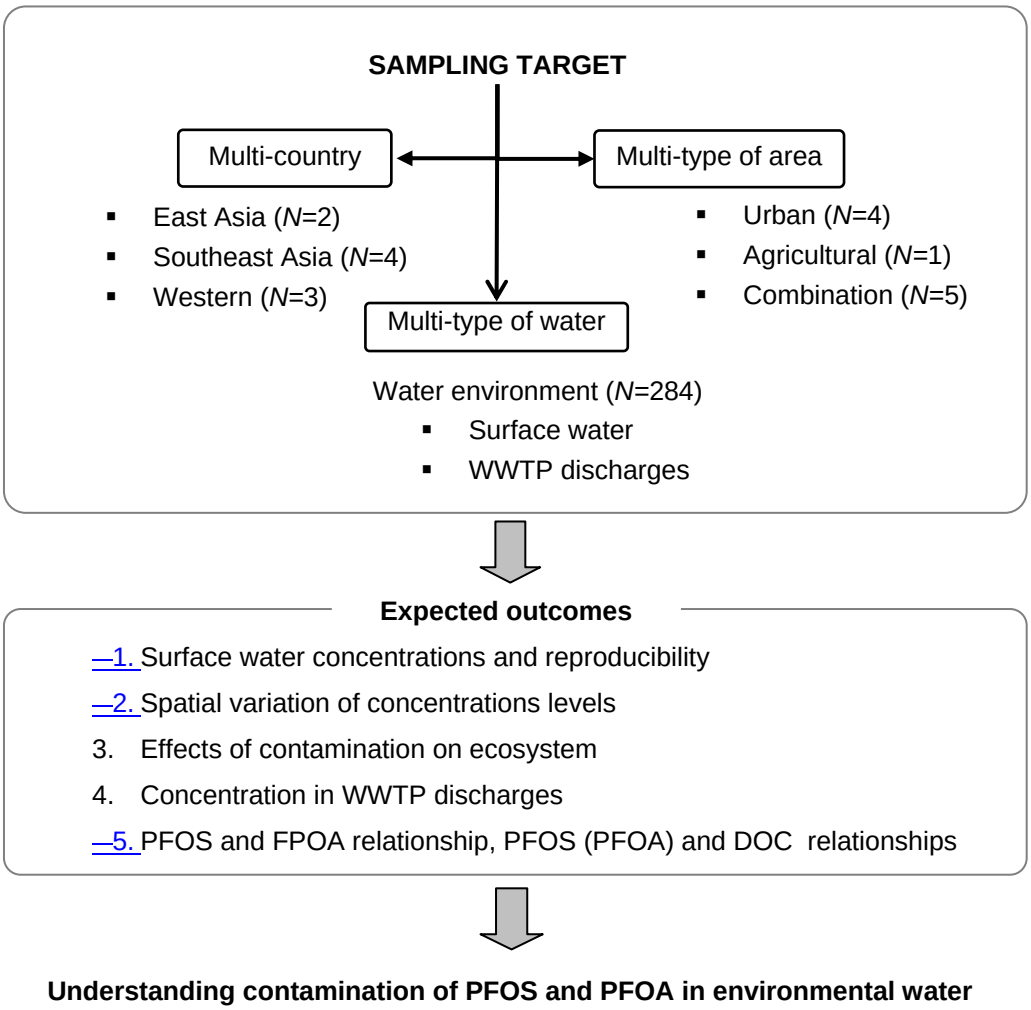

Figure 5.1 A sketch of sampling plan and structure of Chapter V

V.2 MATERIALS AND METHODS

V.2.1 Sampling surveys

Water sampling survey has been described in detail in **Chapter IV.** Survey areas for environmental water sampling in this chapter are shown in **Figure 5.12**. Sampling targeted at various types of surface water collected from rivers, lakes, ponds, reservoirs, wetlands, plash, drainage canal, *etc.* as well as WWTP discharges. Survey areas located in eight

countries including Yodo River (*N*=44) and Kinki (*N*=15) in Japan, Shenzhen (*N*=10) in China, Hanoi (*N*=12) in Vietnam, Phong River (*N*=29) and Chao Phraya River (*N*=15) in Thailand, Kota Kinabalu (*N*=21) and Johor Bahru (*N*=6) in Malaysia, Singapore (*N*=34), Orebro (*N*=16) in Sweden and Turkey (*N*=5). Sampling was conducted during period from November 2004 to December 2006. Repeated sampling was conducted in Yodo River, Phong River and Kota Kinabalu to confirm contamination levels. **Table 5.1** shows characterization of survey areas and summary of sampling. It is also shows Codes of survey areas that will be added as prefix to the number when identifying sampling locations.

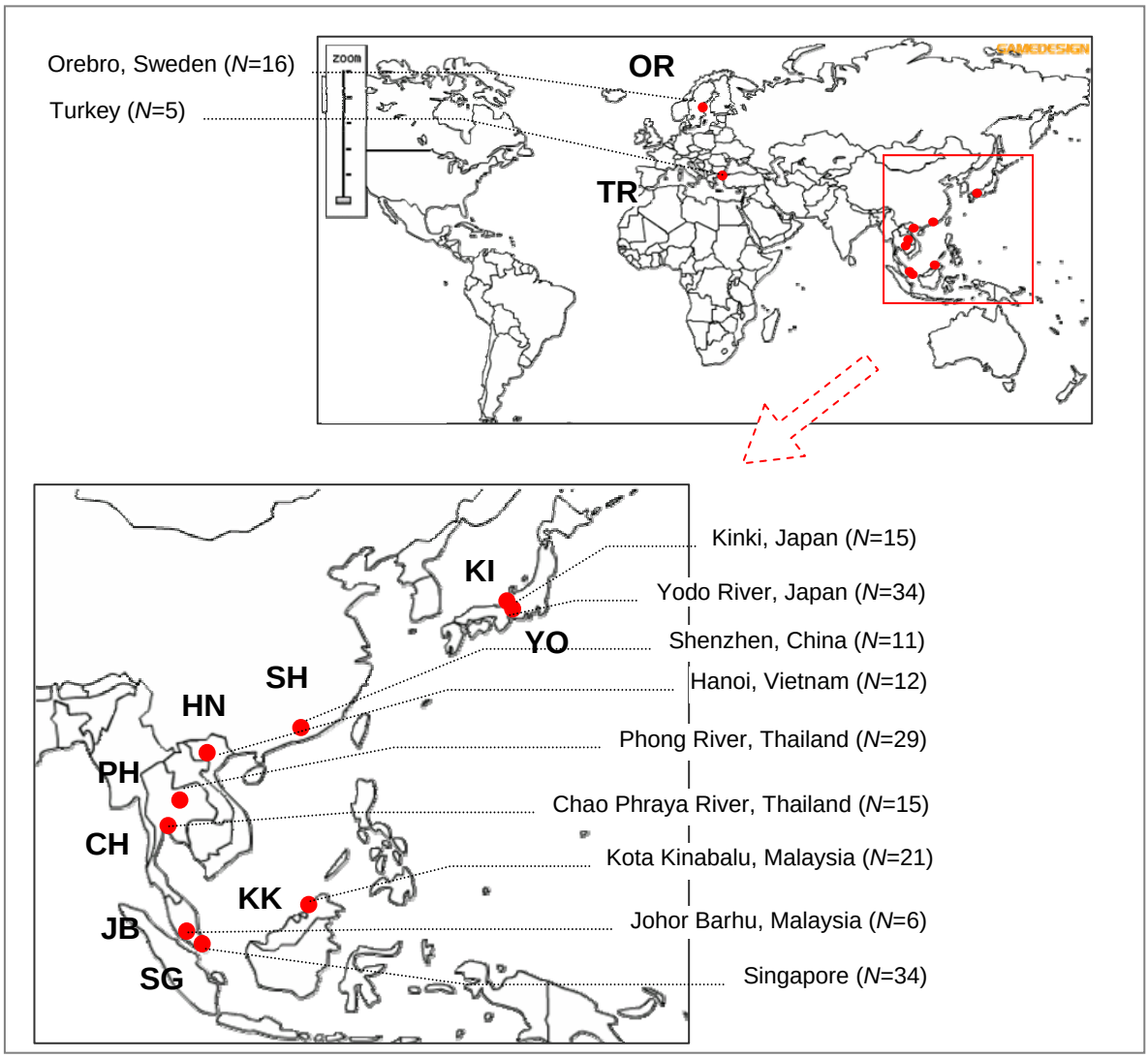

Figure 5.2 Sampling locations of environmental water

Table 5.1 Characterization of survey areas and water sampling

			Survey area charaterization				Water sampling	
	Name	Code	Type of area	Land area	Population	Population density (inh/km^2)	Surface water	WWTP discharge
1	Yodo River	YO	Urban	8,240 (Catchment area)	11,000,000 (2007)	1,335	River	Y*[3]
2	Kinki*[1]	KI	Combination	31,517 (Region)	21,685,000 (2002)	-	River	
3	Shenzhen	SH	Urban	465 (Urban)	8,000,000 (2005)	17,200	Variety*[2]	Y
4	Hanoi	HN	Urban	921 (Urban)	3,145,300 (2005)	3,348	Variety	
5	Phong River	PH	Rural	15,059 (Catchment area)	1,617,000 (2005)	107	River	
6	Chao Phraya River	CH	Combination	21,521 (Catchment area)	11,500,000 (2002)	533	River	
7	Kota Kinabalu	KK	Combination	351 (City)	532,129 (2007)	1,516	Variety	
8	Johor Bahru	JB	Combination	1,871 (District)	1,278,000 (2001)	703	River	
9	Singapore	SG	Urban	704 (Country)	4,483,900 (2006)	6,369	Variety	Y
10	Orebro	OR	Combination	1,380 (Municipality)	128,977 (2006)	93	Variety	Y
11	Tukey (Istanbul)	TR	Combination	-	-	-	Variety	Y

*Note: *[1] Kinki indicates Kinki excluding Yodo River system while sampling; * various kind of water: fresh water (rivers, lakes, ponds, reservoir, etc) and coastal water; *[3] sampling was conducted*

V.2.2 Water analysis

Sampling and analysis method has been described in **Chapter III** and **IV**. Generally, for a PFOS and PFOA measurement, collection of 1L to 2L sample in a PET bottle is needed. Samples collected outside Japan were pre-treated before transportation to Japan in order to continue extraction and quantification. PFOS and PFOA were quantified by solid phase extraction (SPE) coupled with LC/MS analysis.

For samples collected in Yodo River, fundamental water quality items were measured for all of the samples. Total dissolved organic carbon (DOC) was measured by TOC-5000A

(SHIMADZU) and chloride was measured by DX-500 Ion Chromatography system (DIONEX).

V.2.3 Data analysis

Median and standard deviations were calculated. When indicated, the geometric mean (GM) and geometric standard deviation (GSD) were calculated. Values of less than (LOQ) are assumed as half of (LOQ) values for calculations as well as for graph display.

Data analysis also uses clustering analysis and *t*-test. When indicated, clustering analysis uses Euclidean distance and Ward method. For *t*-test, it applies analysis of two samples assuming unequal variances, α=0.05. When p<0.05, the difference is considered to be significant.

V.3 RESULTS AND DISCUSSIONS

V.3.1 Surface water concentrations in individual survey areas

PFOS and PFOA concentration in individual sampling areas will be shown and discussed below. The concentrations are of single sample for sampling location in Kinki, Shenzhen, Hanoi, Chao Phraya River, Johor Bahru and Singapore, while average result are shown for samples collected in Yodo River, Phong River basin and Kota Kinabalu where repeated sampling were conducted. Concentrations below method quantification (LOQ) are shown as ND (non-detectable), and assumed to be half of LOQ for calculation.

V.3.1.1 Yodo River (Japan)

Survey in Yodo River were conducted three times (Nov-04, Mar-05 and Nov-05). Average concentration at individual sampling locations PFOS and PFOA are shown in **Figure 5.3**. PFOS and PFOA were detected in all collected samples of the three sampling dates. Concentrations fluctuated largely throughout the sampling area, in the range of several ng/L up to μg/L level. The range of PFOS concentration (ng/L) in three sampling dates were 0.6 - 50 ng/L, 0.4 -56 ng/L, and 0.8 - 123 ng/L respectively while those of PFOA were 4.2 - 18,300 ng/L, 7.4 - 36,800 ng/L, and 6.0 - 42,000 ng/L correspondingly.

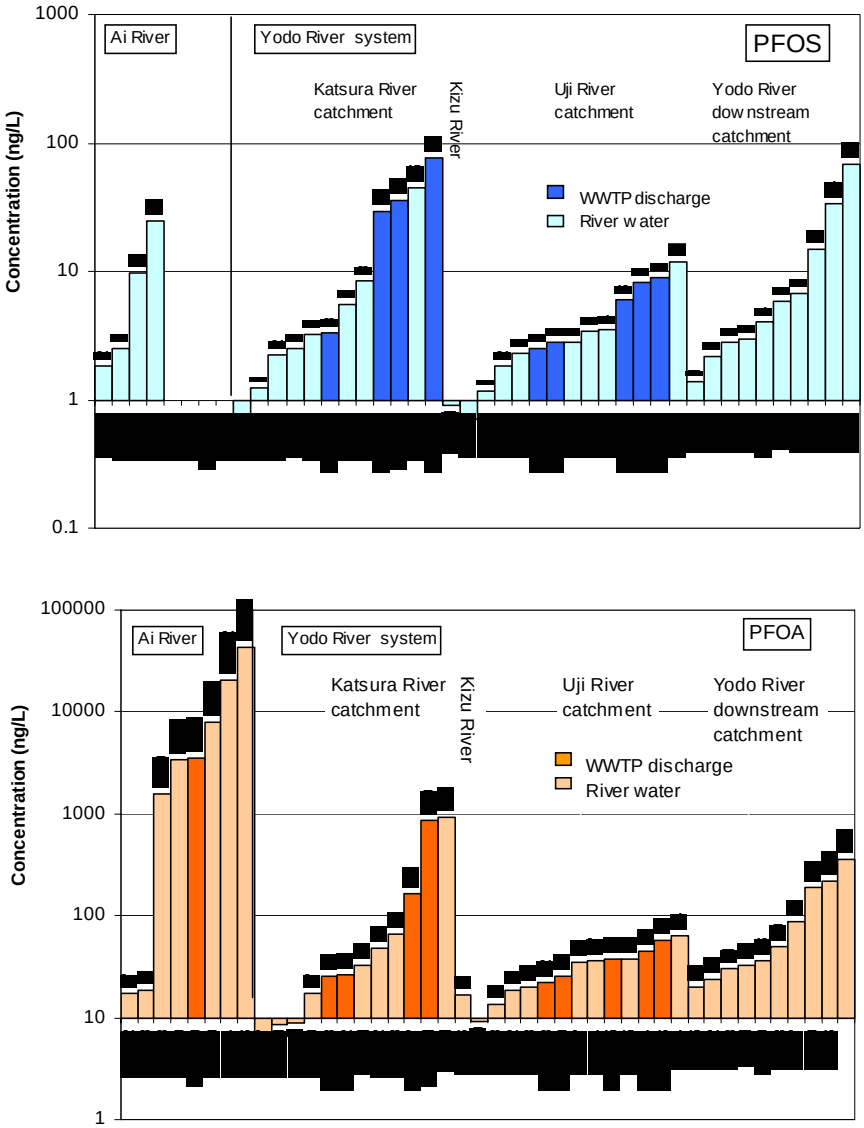

Figure 5.3 PFOS and PFOA concentration in Kinki (Japan)

Low and high levels of PFOS seemed to distribute throughout the basin with highest levels PFOS concentration range of 37 - 116 ng/L, observed mainly in Katsura basin and Yodo downstream tributaries. Highest concentration in surface water of Katsura basin were found in location KA - 23 in Nishi Takase River, at a concentration of 44.6 ng/L. The river is a tributary of Katsura River and its flows was largely contributed by WWTP discharge KA-07. High concentrations were also found in this effluent at an average concentration of 76.4 ng/L and a maximum concentration of 123 ng/L.

Similarly, relatively low concentrations were distributed throughout the basin while high levels of concentration were found in all sub-basins except for Uji sub-basin. Exceptionally high concentrations of PFOA (at three sampling locations) were found only in Ai River at with the concentration fluctuated in the range of up to 5,400 - 46,900 ng/L. This concentration in fact are thousands of time higher than highest levels found for PFOS which is in the range of 37 - 116 ng/L.

In Ai River, while low concentration observed in locations upstream of WWTP discharge AI - W10, all high concentration found in downstream of this WWTPs and in Kanzaki tributary as well. Kanzaki tributary receive partly water from Yodo River basin but the concentration in Yodo River going to this river is relatively low (YO - 03) at average concentration 33 ng/L. High concentration were also observed in AI - 34, Ajiu canal, a tributary to Kanzaki River. Therefore, source of PFOA in Ai River is suppected both WWTPs discharges and Ajiu canal.

It is notable that, WWTP discharges often had relatively high PFOS and PFOA concentration. Among nine investigated WWTPs discharges, except for three effluents had moderate contamination levels the other six effluents had relatively high concentrations. Among those effuents, lower concentrations were found in several WWTP effuents of Uji sub-basin compared to those of Katsura sub-basin

For mainstream water, concentrations of PFOS in Yodo River were measured at 2.2-5.8 ng/L which were close to average values of concentration in the basin. Concentration of PFOA in main stream Yodo River fluctuated around 30 ng/L which were tens times higher than those of PFOS.

V.3.1.2 Kinki (Japan)

Concentrations of PFOS and PFOA in Kinki rivers excluding Yodo River are shown in **Figure 5.4**. The concentrations ranged in 0.27- 13.2 ng/L PFOS and in 0.4-29.9 ng/L PFOA. Therefore, the concentration comparable with Ai River downstream were not found. Relatively low concentrations were often observed in samples collected in upstream and dam sites while relatively high concentrations were often found in samples collected in downstream sites. For examples, samples collected in relative upstream and downstream in Ina River had concentrations from 1.9 to 13.2 ng/L PFOS and from 2.5 to 16.8 ng/L PFOA.

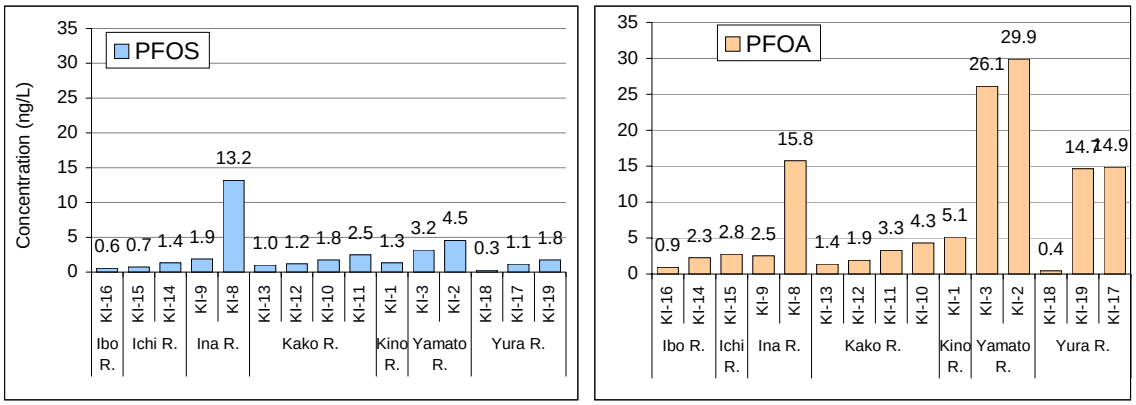

Figure 5.4 PFOS and PFOA concentration in Kinki (Japan) excluding Yodo River

The concentrations were relatively high in Yamato River at 3.2-4.5 ng/L PFOS and 26.1-29.9 ng/L PFOA. Those levels were comparable with those of Yodo River downstream. It has been reported concentration of a single sample to be 18 ng/L PFOS and 41.6 ng/L PFOA in the river (at Suminoe) (Saito *et al.* 2004). Highest concentration of PFOS of 13.2 ng/L PFOS were measured in a sample collected from Ina River downstream was higher than those in downstream sites of Yodo River and comparable with those of Ai River.

V.3.1.3 Shenzhen (China)

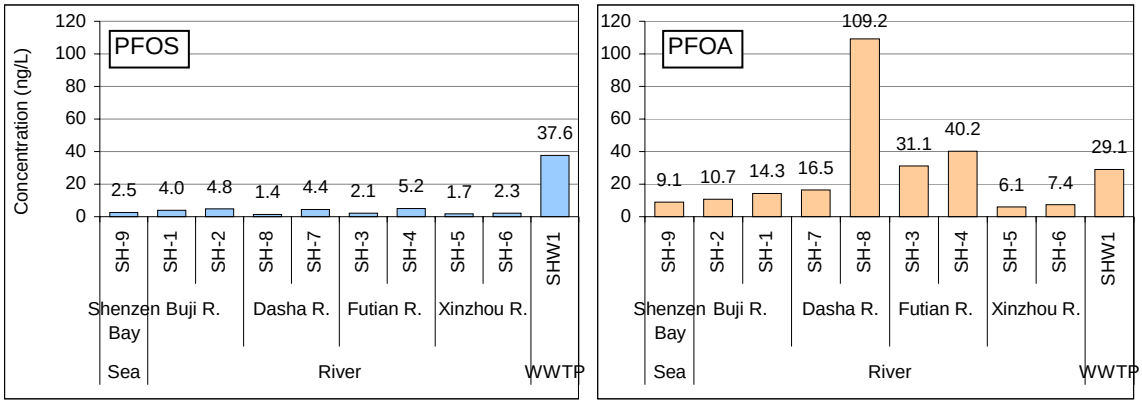

Figure 5.5 PFOS and PFOA concentration in Shenzhen (China)

Collected samples in Shenzhen were detected with PFOS and PFOA well above quantification limits. PFOS concentration ranged 1.4-5.2 ng/L while PFOA ranged 6.1-109.2 ng/L. PFOA concentrations were several times higher than those of PFOS in all of the samples.

Concentrations of both PFOS and PFOA were not significantly different between two sampling locations of Buji River, Futian River, and Xinzhou River. PFOA levels were relatively higher in Futian River (31.1 - 40.2 ng/L) and lower in Xinzhou River (6.1 - 7.4 ng/L). In Dashar River PFOA concentration increased significantly from 16.5 to 109.2 ng/L while PFOS concentration reduced slightly.

A coastal water sample in Shenzhen Bay had concentration of 2.5 ng/L PFOS and 9.1 ng/L PFOA. This value is close to values reported by So *et al.* (2004) of 3.0-3.1 ng/L PFOS and 4.9-5.5 ng/L PFOA in a location (HK6) in western coastal Hong Kong which is about 4 km far from our sampling location. These concentrations were indicated as highest concentrations of both PFOS and PFOA among 6 sampling locations in Hong Kong coast.

V.3.1.4 Hanoi (Vietnam)

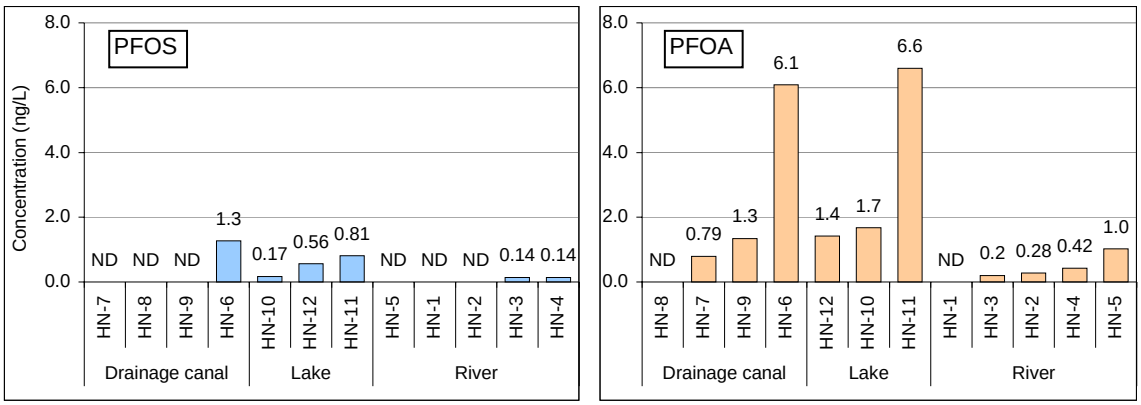

Figure 5.6 PFOS and PFOA concentration in Hanoi (Vietnam)

Half of the collected samples in Hanoi were detected with PFOS (6/12) while most of them were detected with PFOA (10/12). For the samples detected with PFOS, concentrations are actually just above quantification limits with a maximum value of 1.27 ng/L. PFOA concentrations seem to be higher than those of PFOS, with a maximum value of 6.6 ng/L in Hoan Kiem Lake.

Although low concentrations were measured, PFOA concentrations increased slightly from upstream to downstream of Nhue River (0.2-1.03 ng/L) and To Lich canal (ND-1.34 ng/L). Increased concentrations might be related with wastewater discharged from many factories into To Lich canal which finally goes to Nhue River.

Both PFOS and PFOA were detected in all three lake water samples. PFOA concentrations in Hanoi lakes ranged from 1.42 to 6.6 ng/L which was still relatively lower than those of Yodo River and Shenzhen but remarkably higher (ten times) than those in remote lakes in Minnestota, USA (0.14 ng/L to 0.66 ng/L) (Simcik *et al.*, 2005).

V.3.1.5 Phong River (Thailand)

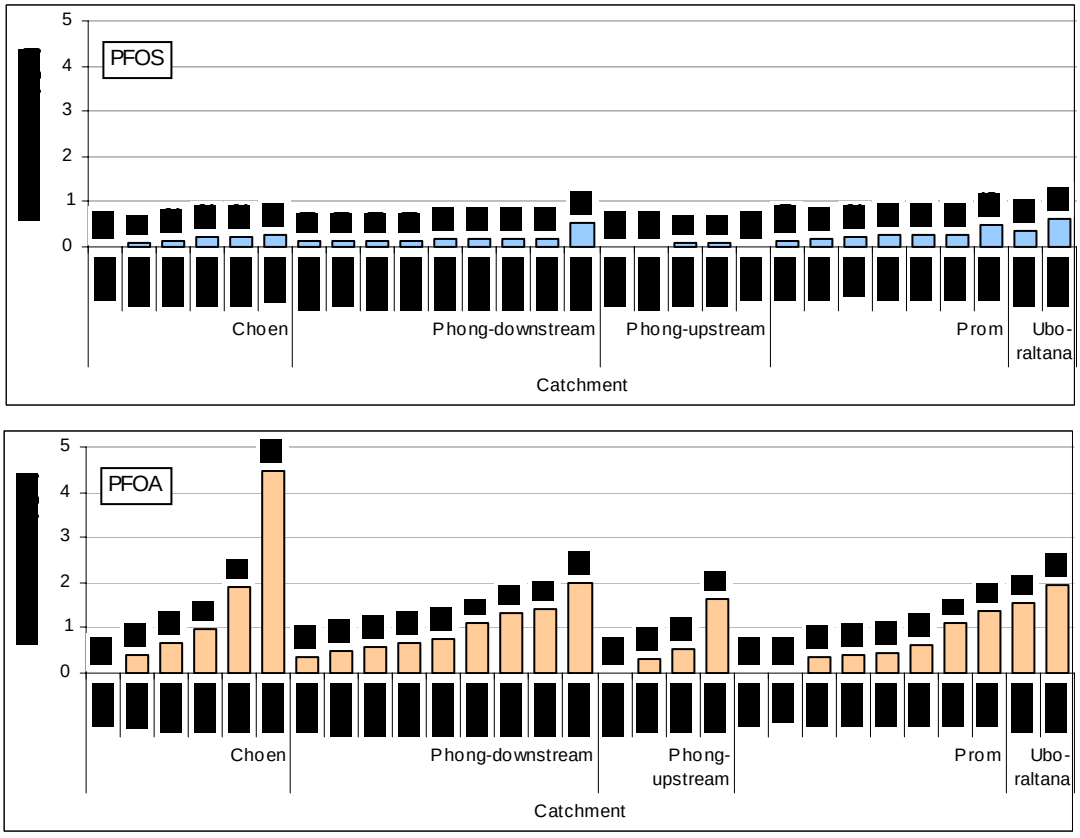

Figure 5.7 PFOS and PFOA concentration in Phong River (Thailand)

More than half of Phong River basin samples had concentrations above LOQ (25/28 and 7/18 for PFOS; and 24/28 and 12/18 for PFOA in the first and second survey respectively). Average concentrations of two sampling periods fluctuated within ND-0.61 ng/L PFOS and ND-4.48 ng/L PFOA.

Non-measurable concentrations were found only in upstream basins (Phong upstream basin, Prom River basin and Choen River basin). In Phong downstream basin, concentration were detectable in both sampling periods with concentrations in the ranges of 0.07-0.91 ng/L

PFOS and 0.16-1.99 ng/L PFOA. Those concentrations was just above the LOQs. Elevated concentration that might indicate point source was not observed.

Concentration in the first survey (rainy season) were slightly higher than in the second survey (dry season) for almost sampling locations that had repeated sampling. Highest concentration in the dry season were 0.91 ng/L PFOS and 1.13 ng/L PFOA.

V.3.1.6 Chao Phraya River (Thailand)

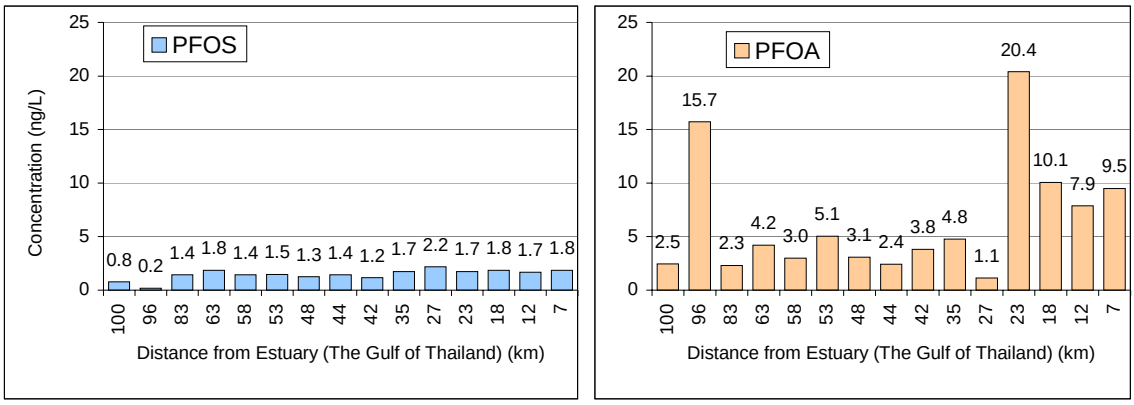

Figure 5.8 PFOS and PFOA concentration in Chao Phraya River (Thailand)

Different from Phong River in northern part of Thailand, samples collected in Chao Phraya River mainstream were all detected with PFOS and PFOA. Concentrations ranged from 0.19-2.2 ng/L PFOS and 1.1 - 20.4 ng/L PFOA.

Along approximately 100 km along Chao Phraya River from the Gulf of Thailand, two peaks of PFOA concentration were found. The first peak was observed in location CH-15, (pumping place of Samlea Water Supply, 96 km far from the Gulf of Thailand) at 15.7 ng/L, but the concentration reduce sharply in the next downstream sampling locations. The second peak were observed at location CH-4 (Wat Yotinpradit 23 km far from the Gulf of Thailand) at 20.4 ng/L while levels of 1.13-4.78 ng/L were observed in 9 upstream sampling locations (CH-5 to CH-14). Downstream of this peak, concentration reduced about half, at 7.9-10.1 ng/L, in three sampling points located at 18, 12, and 7 km far from the Gulf of Thailand) but still elevated compared to those of relative upstream locations.

Different from PFOA, PFOS fluctuated more slightly, ending at the level of 1.68-1.84 ng/L in the most three downstream sampling locations. Lowest levels were observed at 0.19 and

0.79 ng/L in the most two upstream sampling locations. This is the first report of PFOS and PFOA concentration in Chao Phraya River. High concentration of PFOA downstream of river might be related with urban and industrial areas in downstream of the river.

V.3.1.7 Kota Kinabalu (Malaysia)

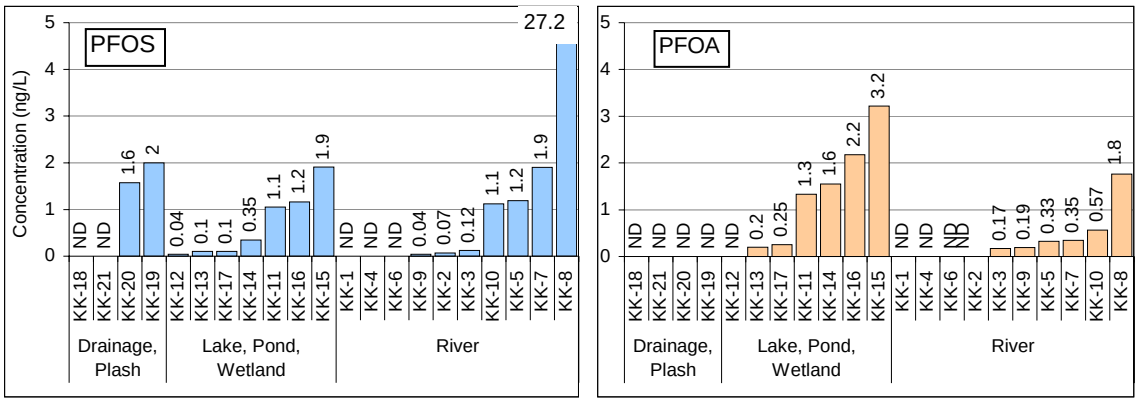

Figure 5.9 PFOS and PFOA concentration in Kota Kinabalu (Malaysia)

PFOS were detected in 14/18 samples and 7/12 samples while PFOA were detected in 10/18 and 5/12 samples, in Sep-05 and Jun-06 respectively. Average concentration in two period ranged ND-27.8 ng/L PFOS and ND-3.32 ng/L PFOA.

Except for samples in location KK-8, which have PFOS concentrations of 3.4 and 52.2 ng/L PFOS in two sampling times, concentration of PFOS ranged ND-2 ng/L and ND-2.2 ng/L respectively. KK-8 is a downstream site of a river near Kota Kinabalu Airport, and both sampling showed elevated concentration compared to upstream (1.56 and 2.24 ng/L in two sampling times). The increasing concentrations not only observed for PFOS but also for PFOA (ND-0.48 ng/L and 0.64-3.03 ng/L in two sampling time). It was before pointed out in Osaka, Japan elevated concentrations of PFOS in surface water around an airport with the concentration up to 500 ng/L.

Sample collected along Inanam River showed slightly increased concentration of PFOS concentrations. Drain and plash samples in the area were not detected with PFOA but with PFOS at the concentrations of 1.6 ng/L and 2.0 ng/L. These two detected samples were both in center of Kota Kinabalu city.

V.3.1.8 Johor Bahru (Malaysia)

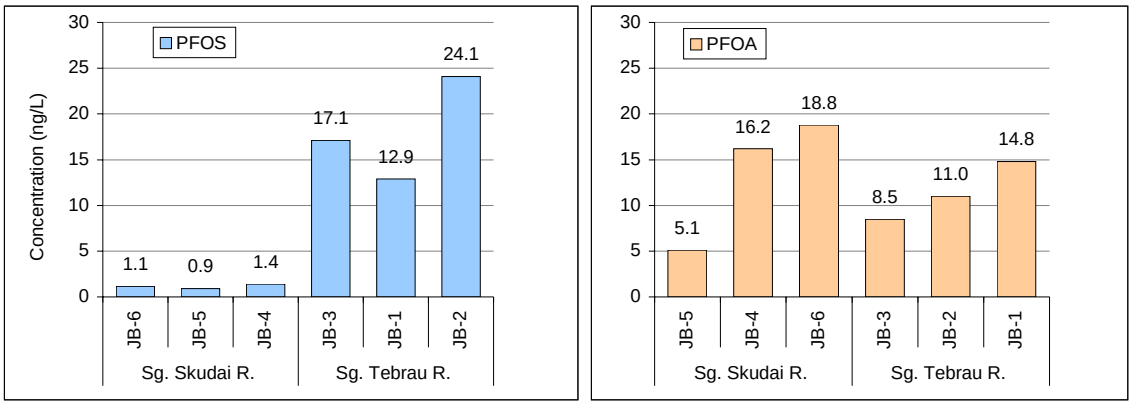

Figure 5.10 PFOS and PFOA concentration in Johor Barhu (Malaysia)

Concentrations ranged 0.9 - 24.1 ng/L PFOS and 5.1 - 18.9 ng/L PFOA in six sampling locations in Sungai Tebrau River and Sungai Skudai River. PFOS concentration were higher in Tebrau (12.9 - 17.1 ng/L) compared to those in Skudai (0.9-1.4 ng/L) which might indicated significant source in Tebrau.

Level of PFOS in Sungai Tebrau were higher than those detected in Chao Phraya River, Phong River, Hanoi, or most of samples in Kota Kinabalu, and quite comparable with highest levels of river water in Yodo River basin.

V.3.1.9 Singapore

Concentrations ranged 0.4-26.5 ng/L PFOS and 0.7-184 ng/L PFOA with medians of 4.7 and 14.2 ng/L for PFOS and PFOA respectively.

Concentrations in reservoir water fluctuated 2.3-26.5 ng/L PFOS and 2.1-43.2 ng/L PFOA Highest concentration for reservoir water was found at 26.5 ng/L PFOS and 43.2 ng/L PFOA in a sample collected in Lower Seletar Reservoir. Lowest concentration of PFOS in Resevoir water samples which were at 2.3 ng/L is in fact higher than maximum concentration found in collected samples in Hanoi, Phong River, Orebro and Turkey.

Concentrations in stream water fluctuated 0.63-23.5 ng/L PFOS and 6.82-184.3 ng/L PFOA. Therefore, the concentration range of PFOS were comparable with those of reservoir water. Highest concentrations of PFOA were several times higher than those of reservoir water.

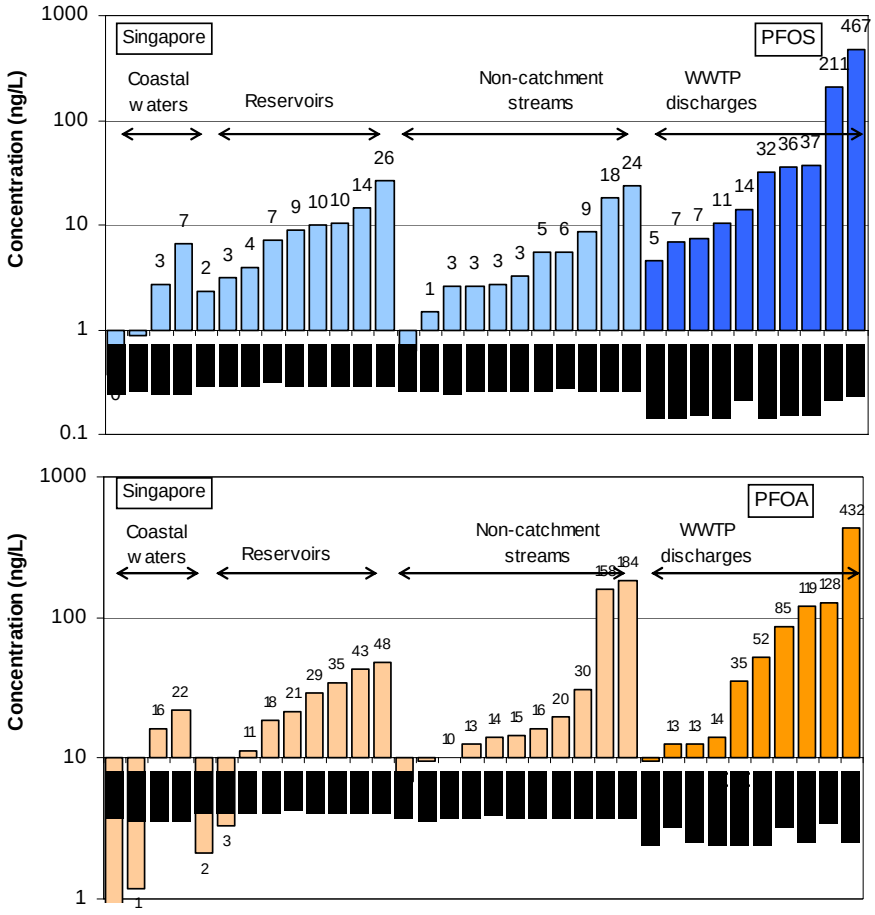

Figure 5.11 PFOS and PFOA concentration in Singapore

Coastal water samples collected in Singapore Straits and Johor Straits showed contamination of both PFOS and PFOA. Relatively high contamination levels were found in water sample collected form Singapore Bay and a water sample collected in Johor Strait. The contamination in Singapore Bay is possibly due to discharge from Singapore water Contamination seemed to be diluted when go to Singapore Strait (SG-23 in Marina South) with the concentration of 0.4 ng/L PFOS and 1.2 ng/L PFOA. On the other hand, contamination in Johor Straits contamination could also due to contamination of Johor water since relatively high concentrations of both PFOS and PFOA were observed in at least two rivers from Johor State.

V.3.1.10 Orebro (Sweden)

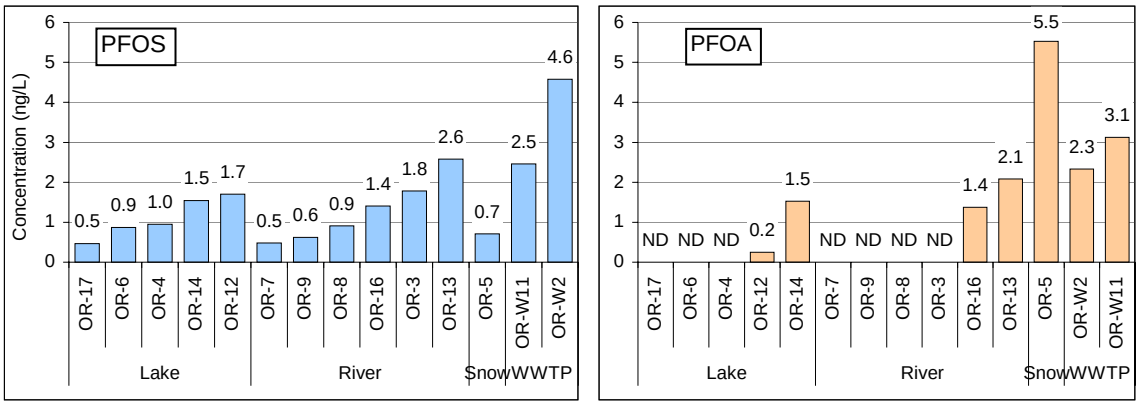

Figure 5.12 PFOS and PFOA concentration in Orebro (Sweden)

Concentrations are shown in **Table 5.12**. PFOS were detected in all collected samples with the concentration ranged 0.46-2.6 ng/L while PFOA were detected in 5/12 samples at maximum concentration of 5.53 ng/L. Among 5 samples detected with PFOA, 3 samples collected near paper factory. Highest concentrations of PFOA of 5.53 ng/L were a snow sample collected in a ski center.

V.3.1.11 Turkey

Concentrations are shown in **Table 5.13**. All samples detected with PFOS and PFOA typically at several ng/L. PFOA was measured at concentrations higher than PFOS. Highest concentration of PFOA were measured in a sample collected from a WWTP discharge.

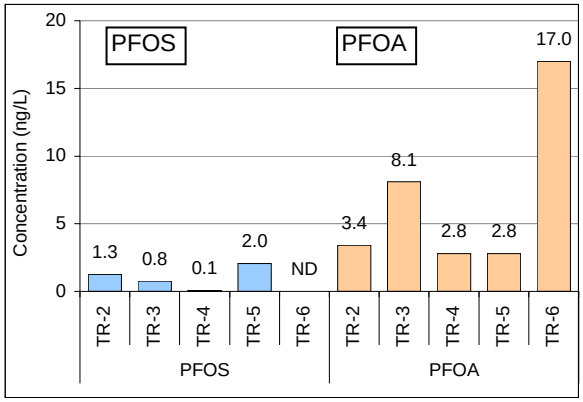

Figure 5.13 PFOS and PFOA concentration in Turkey

V.3.1.12 Reproducibility of concentrations among repeated samplings

Repeated sampling was conducted in three areas: Yodo River system (Japan), Phong River system (Thailand) and Kota Kinabalu (Malaysia). Sampling surveys in Yodo River systems were conducted three times, starting with a survey in Nov 2005, followed by other surveys with interval of approximately 4 month to the second survey and another 7 month

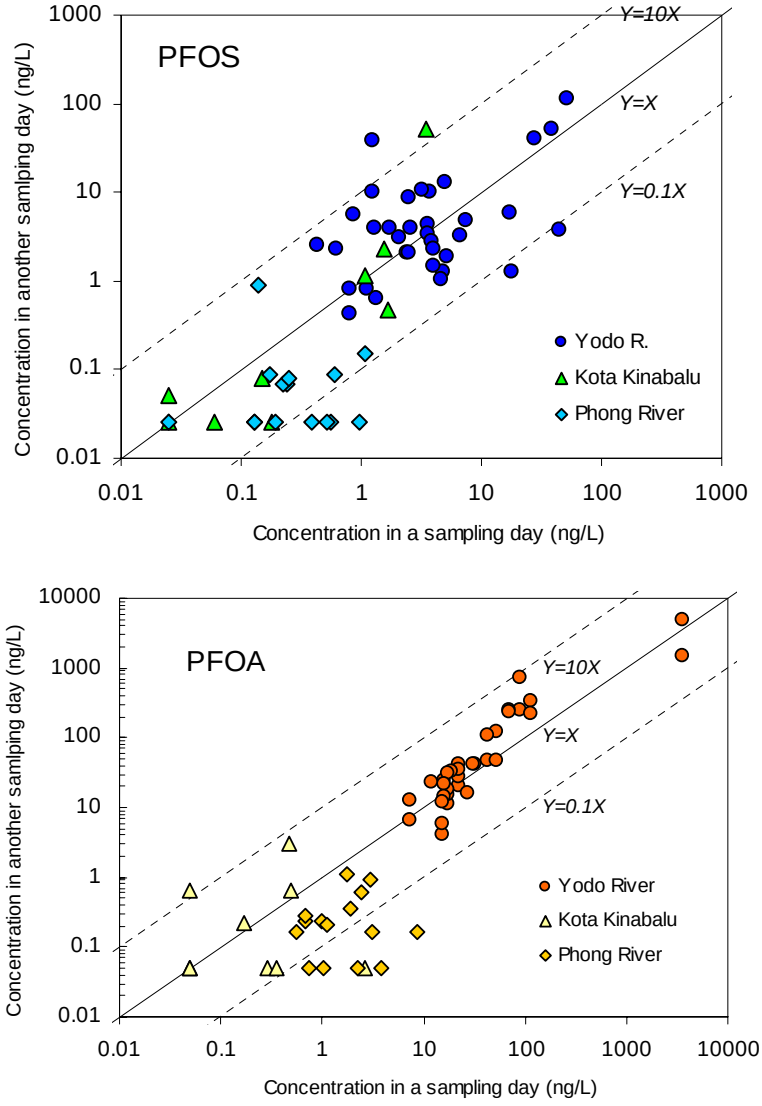

Figure 5.14 Concentrations in one sampling day versus another sampling day

to the third survey. All surveys were conducted in days when no rain event was observed. Sampling surveys in Phong River was conducted twice, in rainy season (Jul 2005) and dry season (Jan 2006). Sampling surveys in Kota Kinabalu were conducted twice with two month interval (Aug-Sep 2005 and Nov 2005).

Figure 5.14 plots concentration in a sampling date versus another sampling dates. Plots fluctuate around linear line 1:1 and the differences are generally less than one order of magnitude as shown in the figure. Fluctuation of concentration especially is less significant for higher concentrations.

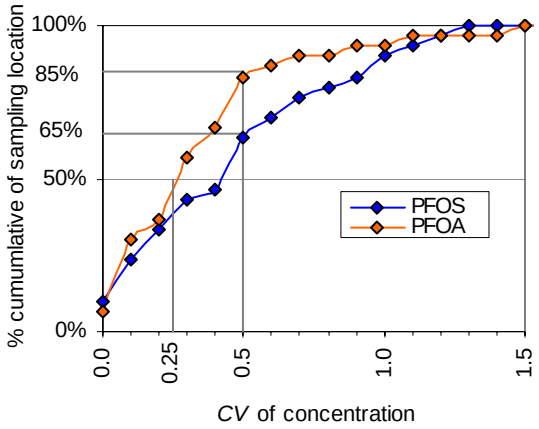

Figure 5.15 Cummulative number of sampling locations vs. *CV* of concentrations

In Yodo River, fluctuation of concentration in different sampling dates was evaluated based on coefficient of variation of concentration (*CV*). **Figure 5.16** summaries number of sampling locations based on CV values which indicated that about 50% of sampling locations that have repeated sampling have CV values less than 0.25 indicating relatively low variation of concentrations. Approximately 85% and 65% number of sampling locations have CV less than 0.5 respectively for PFOS and PFOA. Less than 10% of sampling locations (a few sampling locations) have CV above one. This suggests the significant reproducibility of both PFOS and PFOA concentrations in the Yodo River water

Although the primary supplier of PFOS, its salts and its precursors (3M Company) phased out the production of these substances in 2002, PFOS was still repeatedly detected with the comparable levels. This implies that PFOS and/or PFOS-related chemicals are still in use or present in applicable products and that the implication do not conflicts with information provided by OECD (2005) (**Chapter II)**.

It was indicated that human exposure to both PFOS and PFOA was more extensive in the Kinki district than in other studied areas such as Akita, Miyagi (Harada *et al.* 2004). Since Yodo River surface water is the source of tap water for about 11 million people in Kinki, long-term contamination of surface water might result in levels in drinking water that increase human exposure through drinking pathways.

V.3.2 Spatial differences of surface water concentration levels

This section discusses spatial difference in surface water concentration levels. Firstly, statistical summaries of surface water concentrations in individual sampling areas are shown and compared (**V.3.3.1**). Secondly, further discussion in differences of concentration levels in relation with characterizations of survey areas will be shown (**V.3.3.2**). Finally, comparison of concentrations found in this study with those reported in

literature will be discussed (**V.3.3.3**). Discussion on concentrations in WWTP discharges will be shown separately.

V.3.2.1 Statistical summary of surface water concentrations

Table 5.2 Statistic description of PFOS concentrations (ng/L)

Sampling area			N	Min	Max	Median	GM	Mean	STD
1	YO	Yodo River	34	0.56	67.4	3.5	4.9	10.8	2.6
2	KI	Kinki	15	0.27	13.2	1.5	1.6	2.4	0.8
3	SH	Shenzhen	9	1.42	5.2	2.5	2.9	3.1	0.5
4	HN	Hanoi	12	0.03	1.3	0.1	0.1	0.3	0.1
5	PH	Phong River	29	0.03	0.6	0.2	0.2	0.2	0.0
6	CH	Chao Phraya R.	15	0.19	2.2	1.6	1.3	1.5	0.1
7	KK	Kota Kinabalu	21	0.03	27.8	0.1	0.3	1.9	1.3
8	JB	Johor Bahru	6	0.90	24.1	7.1	4.4	9.6	4.1
9	SG	Singapore	24	0.37	26.5	4.7	4.4	7.2	1.5
10	OR	Orebro	12	0.46	2.6	0.9	1.0	1.2	0.2
11	TR	Turkey	4	0.08	2.1	1.0	0.6	1.0	0.4

Note: N: number of sampling locations; Min: minimum; Max: maximum, Geomean:geometric mean, STD: standard deviation

Table 5.3 Statistic description of PFOA concentrations (ng/L)

Sampling area			N	Min	Max	Median	GM	Mean	STD
1	YO	Yodo River	34	6.63	21619.5	34.4	69.1	1540.8	865.1
2	KI	Kinki	15	0.43	29.9	3.3	4.3	8.4	2.5
3	SH	Shenzhen	9	6.07	109.2	14.3	17.3	27.2	10.9
4	HN	Hanoi	12	0.08	6.6	0.9	0.7	1.7	0.7
5	PH	Phong River	29	0.05	4.5	0.7	0.6	1.0	0.2
6	CH	Chao Phraya R.	15	1.13	20.4	4.2	4.7	6.4	1.4
7	KK	Kota Kinabalu	21	0.05	3.2	0.2	0.2	0.6	0.2
8	JB	Johor Bahru	6	5.09	18.9	12.9	11.4	12.4	2.1
9	SG	Singapore	24	0.72	184.0	16.4	14.7	30.3	9.2
10	OR	Orebro	12	0.10	5.5	0.1	0.3	1.0	0.5
11	TR	Turkey	4	2.78	8.1	3.1	3.8	4.3	1.3

Note: N: number of sampling locations; Min: minimum; Max: maximum, GM:geometric mean; STD: standard deviation

In total of 185 surface water sampling locations, 170 locations had sample(s) detected with PFOS and 163 locations had sample(s) detected with PFOA respectively. Therefore, the majority of collected samples were detected with PFOS (91%) and PFOA (88%). As a whole, maximum PFOS concentrations were measured at 67.4 ng/L PFOS (average) samples collected in Yodo River system, followed by 27 ng/L (average) and 26 ng/L PFOS in Kota Kinabalu, and Shenzhen. Maximum PFOA concentration were measured at 21,620 ng/L PFOA (average), followed by 184 ng/L PFOA in Singapore and 109 ng/L in Shenzhen.

Statistical summaries of PFOS and PFOA concentrations in each sampling areas are shown and compared in **Table 5.2** and **Table 5.3** while distribution of the concentration are shown and compared in **Figure 5.16**. Data was shown based on sampling location so that if a sampling location had repeated sampling, average concentrations were used for calculation. Non detectable concentrations are assumed haft of detection limits for data shown and for calculation of statistic values.

Median concentration of PFOS fluctuated from ND levels (<0.05 ng/L) in Hanoi and Phong River to 7.1 ng/L in Johor Bahru while maximum concentration in individual survey areas fluctuated from 0.61 ng/L in Phong River to 67.4 ng/L in Yodo River. In a summary, median (range) of PFOS concentrations in ng/L were 3.4 (0.6-67.4) in Yodo River; 1.4 (0.3-13.2) in Kinki region (excluding Yodo River); 2.5 (1.4-5.2) in Shenzhen; 0.08 (ND-1.3) in Hanoi, 0.16 (ND-0.61) in Phong River; 1.5 (0.2-2.2) in Chao Phraya River; 0.12 (ND-27.8) in Kota Kinabalu; 7.3 (0.9-24.1) in Johor Bahru; 4.7 (0.4-26.5) in Singapore; 0.93 (0.5-26) in Orebro; and 1.0 (0.08-2.15) in Turkey.

Median concentrations of PFOA fluctuated from 0.1 ng/L in Orebro to 34.4 ng/L in Yodo River while maximum concentration fluctuated from 3.2 ng/L in Kota Kinabalu to 21,600 ng/L in Yodo River. Therefore, the ranges of either median or maximum concentrations for PFOA were higher than those for PFOS. In a summary, median (range) of PFOA concentration in ng/L were 34.4 (6.6-21,619) in Yodo River; 3.3 (0.4-30.0) in Kinki (excluding Yodo River); 14.3 (6.1-109.2) in Shenzhen; 0.91 (ND-6.6) in Hanoi; 0.66 (ND-4.5) in Phong River; 4.2 (1.1-20.4) in Chao Phraya River; 0.19 (ND-3.22) in Kota Kinabalu; 12.9 (5.10-18.9) in Johor Bahru; 16.4 (0.7-184) in Singapore; 0.1 (ND-5.53) in Orebro; and 3.1 (2.8-8.1) in Turkey.

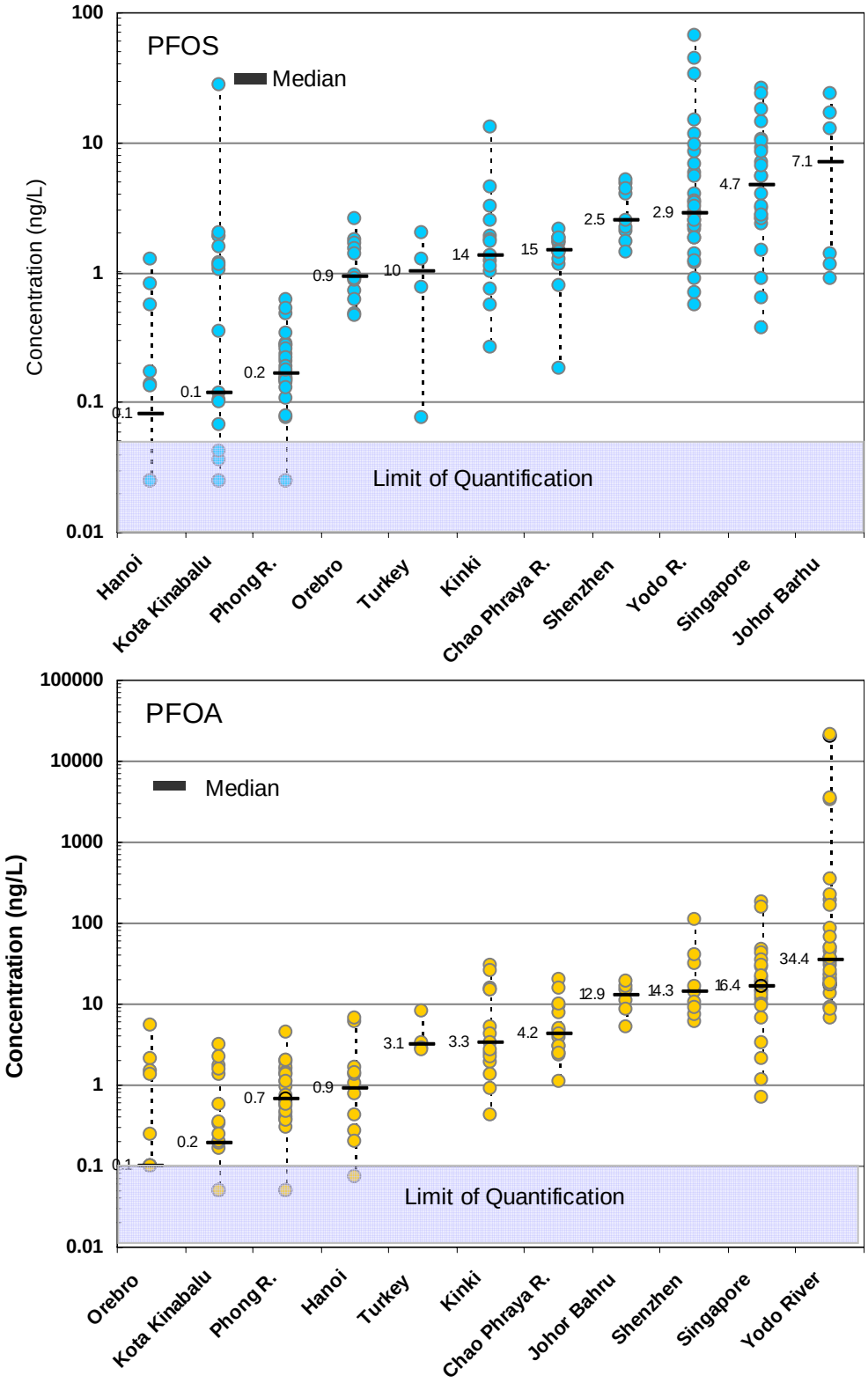

Figure 5.16 Distribution of PFOS and PFOA concentrations in different survey areas

Statistical summary in Table 5.2 and 5.3 shows values of median and geometric mean of concentrations, which seem to be close to each other in individual survey areas. It is found the good linear relationships between median and mean concentration as shown in **Figure 5.17**. Therefore, mean or median values are similar in comparison with the contamination levels among different sampling areas. There is also increasing trend of concentration ranges following increasing median concentration for both PFOS and PFOA as shown in Figure 5.16. Therefore, median concentration is quite appropriate to compare concentration levels among different areas.

If taking median concentration to compare, PFOS concentration levels could be ranked from highest to lowest as follow: Malaysia (Johor Barhu), Singapore, Japan (Yodo R.), China (Shenzhen), Japan (Kinki, except Yodo R.), Thailand (Chao Phraya R.), Turkey (Istanbul and Newsehir), Sweden (Orebro), Thailand (Phong R.), Malaysia (Kota Kinabalu), Vietnam (Hanoi). That of PFOA were Japan (Yodo R.), Singapore, China (Shenzhen), Malaysia (Johor Bahru), Japan (Kinki, except Yodo R.), Thailand (Chao Phraya R.), Turkey (Istanbul, Newsehir), Vietnam (Hanoi), Thailand (Phong R.), Malaysia (Kota Kinabalu), Sweden (Orebro).

V.3.2.2 Spatial differences of concentrations levels

It could be seen fluctuation of concentrations levels in different sampling areas as discussed above. The difference in median concentration were found even in different sampling areas within a country (Japan, Malaysia, Thailand). There should be different

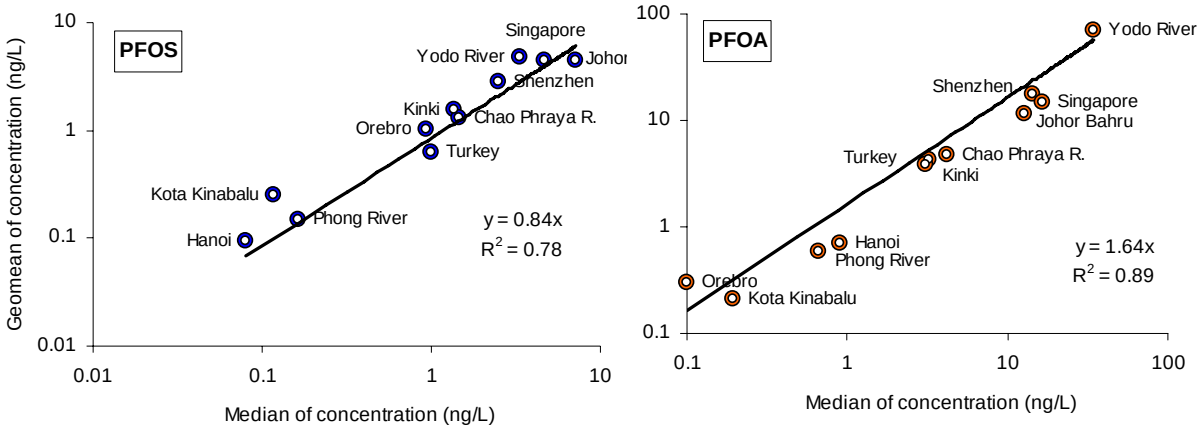

Figure 5.17 Linear relationship between median and geomean of concentrations

production and use pattern of PFOS, PFOA and related perfluorochemicals (PFCs) that cause different in concentration levels. This section shows further discussion in difference of concentration levels by (1) cluster analysis and discussion with regional property and by (2) comparison of concentration levels among survey areas those are located within a country.

(1) ***Classification of survey areas based on concentration levels***

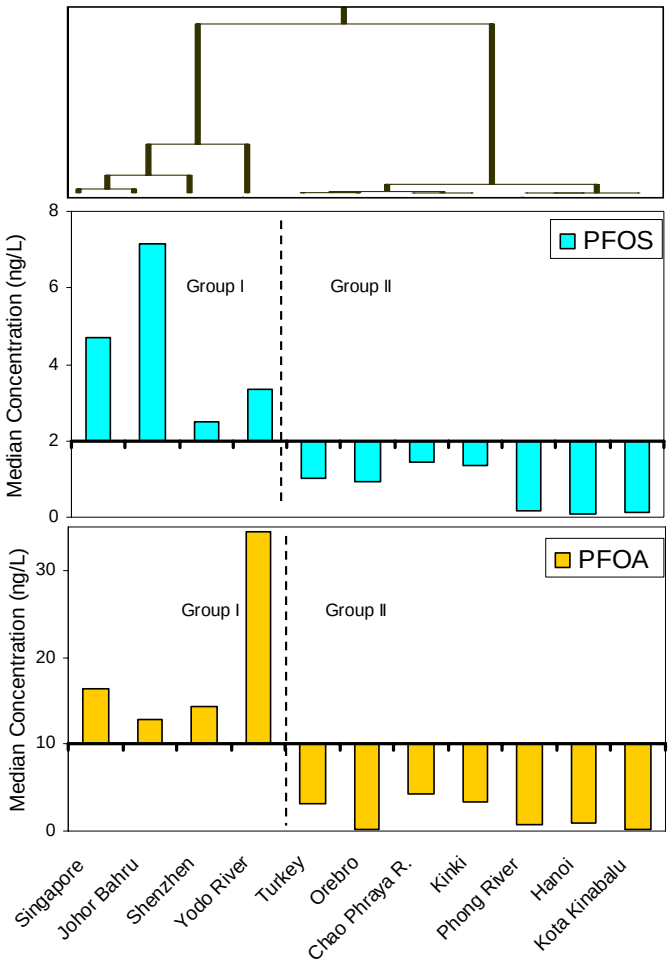

Figure 5.18 Clustering diagram for median concentrations of PFOS and PFOA in individual survey areas

Cluster analysis was simply conducted using median concentrations of PFOS and PFOA concentrations in 11 survey areas. It used Euclidean distance and Ward method. Clustering diagram is shown in **Figure 5.18** together with median concentration of PFOS and PFOA.

Surveys areas could be classified into two groups with significant difference of both PFOS and PFOA concentration: Group I including Yodo River, Shenzhen, Johor Bahru, and Singapore and Group II including the other survey areas of Kinki (excluding Yodo R.) Hanoi, Phong River, Chao Phraya River, Kota Kinaablu, Orebro, Turkey. As shown in Figure 5.18, group I have median concentration higher than 2 ng/L PFOS and 10 ng/L PFOA while group II have median concentration significantly lower.

Survey areas in this study were belong to many types those could be urban or agricultural or combination, it could be densely populated or non-populated. It was observed that survey areas of Group I where relatively high concentration were observed are in fact urbanized and populated areas as shown in Table 5.1. Group II with relatively low level of both PFOS and PFOA including many areas those are either less populated or without increasing industrialization.

Difference in concentrations were observed for PFOA rather than for PFOS. Further discussion between relative contamination of PFOS and PFOA will be discussed latter. PFOA concentration in Yodo River system were higher than the other sampling areas ($p<0.05$, *t*-test). The reason migh in part due to the fact that rivers in Yodo River system run through populated and industrialized areas in Kyoto and Osaka and receives all wastewater from the catchment area. Concentration was also high in WWTP discharges as discussed. Further analysis in Chapter VII will search for sources of the chemicals in Yodo River system.

(2) ***Differences of concentration levels within a country***

Table 5.4 Result of *t*-test for concentrations data set within a country

	PFOS concentration (ng/L)		PFOA concentration (ng/L)	
JAPAN	Yodo R.	Kinki	Yodo R.	Kinki
Mean	8.43	2.42	1540.78	8.41
Observations	30	15	34	15
p(T≤t) two-tail	0.040		0.086	
THAILAND	Phong R	Chao Phraya R.	Phong R	Chao Phraya R.
Mean	0.20	1.47	0.95	6.38
Observations	29	15	29	15
p(T≤t) two-tail	6.4E-08		1.9E-03	
MALAYSIA	Kota Kinabalu	Johor Bahru	Kota Kinabalu	Johor Bahru
Mean	1.94	9.59	0.60	12.41
Observations	21	6	21	6
p(T≤t) two-tail	0.122		0.002	

Difference in the concentration levels were observed among survey areas within a country. They are Yodo River versus Kinki Area in Japan, Johor Bahru versus Kota Kinabalu in Malaysia, and Chao Phraya River versus Phong River in Thailand as shown in Figure 5.18. Data analysis using *t*-test was conducted to examine the difference concentrations and the results are shown in **Table 5.4**.

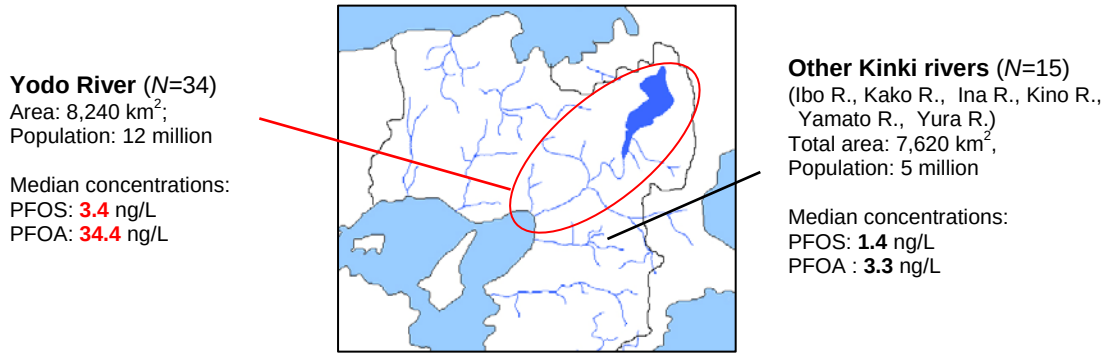

Figure 5.19 Kinki Region and Yodo River system

The table indicated that concentration levels in Yodo River (*N*=34) were quite significantly higher than those for other River system in Kinki areas (*N*=15), (p<0.05 for PFOS and p<0.09 for PFOA). An illustration in **Figure 5.19** shows that Yodo River runs through a populated area compared to those for other rivers in Kinki Area. Yodo River run through area that industrialization was more intensive than that for other rivers.

In Thailand, median concentrations in Chao Phraya River were approximately ten times higher in Phong River with values of 1.5 versus 0.2 ng/L for PFOS and 6.3 versus 0.95 ng/L for PFOA. The difference was significant with p< 0.01 for both PFOS and PFOA. As depicted in **Figure 5.20**, Chao Phraya River runs through both agricultural and industrialized areas while Phong River mainly run through agricultural area. Population density in Chao Phraya River (500 inh/km^2) was about five times higher in Phong River (100 inh/km^2). Relatively high concentration levels in Chao Phraya River might be related with industrialization and urbanization in the river catchment area.

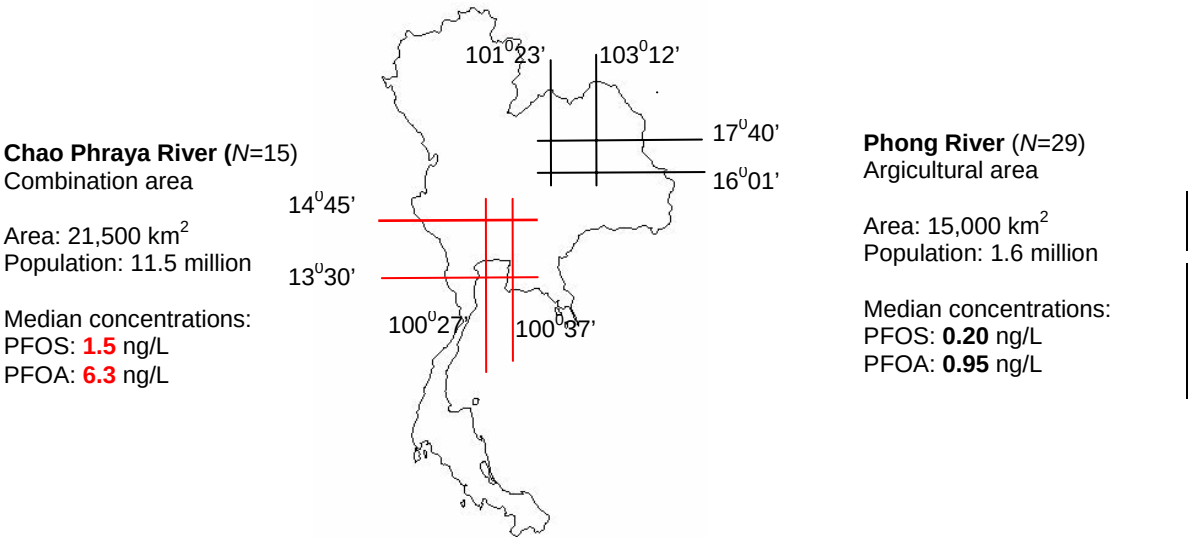

Figure 5.20 Map of Thailand showing two survey areas

In Malaysia, while median concentrations of both PFOS and PFOA were about ten times higher in Johor Bahru compared to Kota Kinabalu (7.1 versus 0.1 ng/L PFOS and 12.9 versus 0.2 ng/L PFOA), the difference were significant only for PFOA (p<0.001). Both Johor Barhu and Kota Kinabalu are fast developed and urbanized in the last decades but Johor Bahru is an industrialized area while Kota Kinabalu is a natural conservative area being commercialized. High contamination levels of PFOA in Johor Bahru might related with industrialization there.

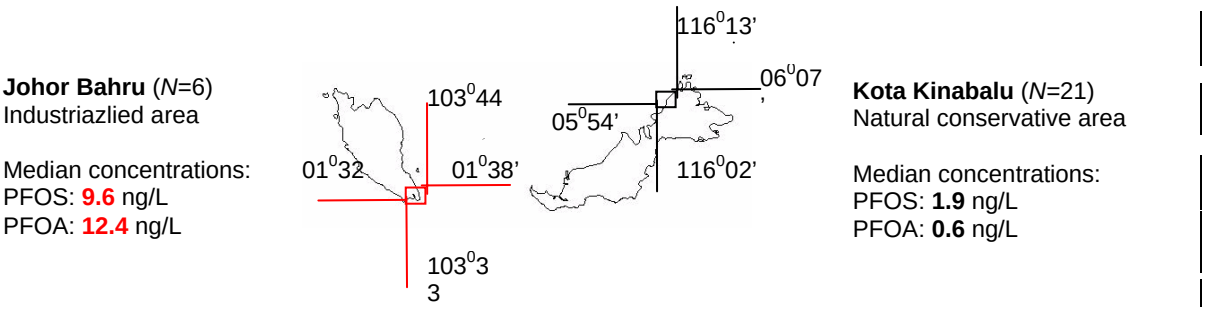

Figure 5.21 Map of Malaysia showing two survey areas

As a conclusion, differences in concentrations of both PFOS and PFOA were found significantly among different survey areas within a country as demonstrated in Japan, Thailand and Malaysia. It is observed that relatively high contamination levels of either PFOS or PFOA were often found in industrialized and urbanized areas.

V.3.2.3 Comparison with other surface waters in literature

In the previous studies, examination of PFOS and PFOA contamination was often conducted in developed countries and urban and industrialized areas. Four sets of reference data in Japan (Saito *et al.* 2004), Michigan and New York in USA (Sinclair *et al.* 2004, 2006) and Nordic Europe (Berger *et al.* 2004) were shown in Figure 5.22 for comparison with concentrations found in this study. It is shown that the medians of concentrations in highly contaminated area (Yodo River, Shenzhen, Johor Bahru and Singapore) were

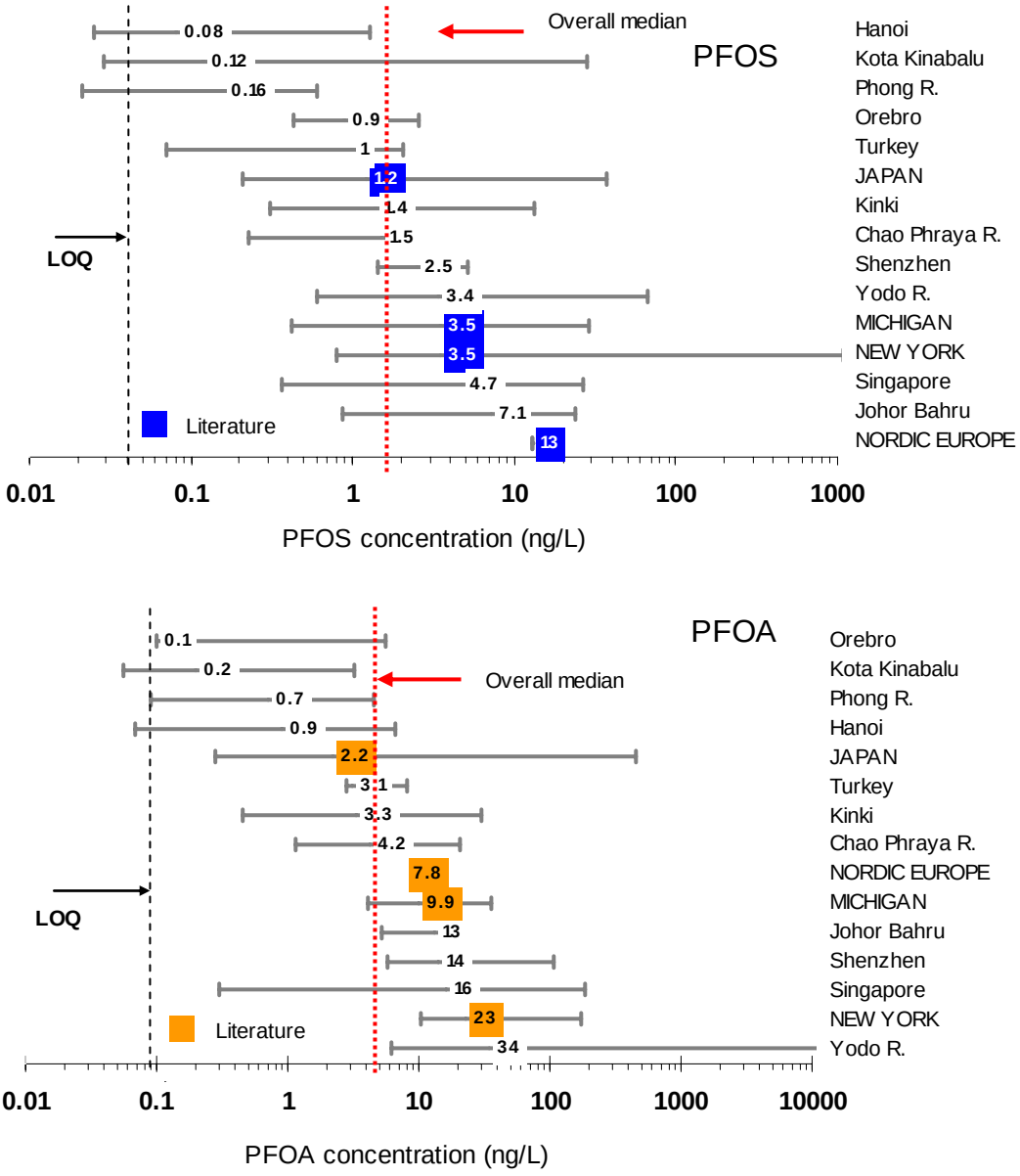

Figure 5.22 Comparison of PFOS and PFOA concentration in this study with data reported from literature

comparable with those in New York State and Michigan State. Average concentrations in downstream sites of Yodo River were 3-4 ng/L for PFOS and 23-33 ng/L for PFOA while they were indicated in another study at 10-11 ng/L and 31-32 ng/L respectively on 2003-04-11 (Saito *et al.* 2004). Therefore, concentration levels were quite comparable.

When comparing median concentration of both PFOS and PFOA in Orebro (0.9 ng/L PFOS and 0.1 ng/L PFOA) with reported values for Nordic European country which were reported to be 13 ng/L PFOS and 7.8 ng/L PFOA in lakes water, concentration were about ten times lower. However it is indicated that data reported for surface water in urbanized and industrialized areas, different from Orebro, which is slightly urbanized and less populated (population density of 93 inh/km^2).

High levels of hundred ng/L PFOA were observed in Singapore and Yodo River can be comparable with downstream water of Tennesee River (USA), where effluent from a fluorochemical manufactory was suggested to be the source of the contaminants (Hansen *et al.* 2002) (data not shown). However, exceptionally high concentration of PFOA (several ug/L) were not reported in literature except for the case of AFFF application (Moody *et al.* 1999, 2003) (data not shown). PFOA concentration at level of several ten thousand ng/L found in Ai River (Yodo River system) was also in consistent with reported values by Saito *et al.* 2004. This concentration level was not reported elsewhere for surface water so far.

Yamashita *et al.* (2005) measured concentration of PFOS and PFOA in oceanic water of Pacific and Atlantic ocean found the lowest concentration to be in several pg/L. Lowest concentration levels were observed in Phong River, Hanoi, Kota Kinabalu, when compared with background levels in oceanic water, where tens to thousand time higher indicating affect from human activity.

V.3.3 Effects of PFOS and PFOA contamination on ecosystems

A few researches on ecotoxicty of PFOS and PFOA have been reported. A review of aquatic toxicity studies reported that PFOS is moderately acutely toxic and slightly chronically toxic to aquatic organisms (Hekster *et al.* 2003). The lowest observed median lethal concentration LC_{50} (96h) was estimated to be 4.7 mg/l and 3.6 mg/l for lithium salt of PFOS, in fathead minnow (*Pimephales promelas*) and the mysid shrimp (*Mysidopsis bahia)* respectively (OECD 2002). The lowest NOEC, 0.3 mg/l and 0.25 mg/l have been observed in the two species respectively (OECD, 2002). In another study (MacDonald *et*

al. 2004), midge larvae (*Chironomus tentans*) did not survive exposure to 100 µg/l in the water. At doses of 50 µg/L or greater, there was a significant reduction in midge survival, a significant decline in growth and adverse impacts on emergence of adult midges from larvae. Median lethal concentration LC_{50} was 45.2 µg/L, much lower than those of the two species mentioned above. The adverse effects on midges in this study occurred at concentrations that still normally exceed environmental concentrations often found in this study (0.07 µg/L at maximum). However, further toxicity study might be needed to evaluate the other effect of the concentrations found in this study to other species.

In a toxicity study of PFOA on fathead minnow (*Pimephales promelas*) (Oakes *et al.* 2004), exposure to water concentrations of 0.3 mg/L (300 µg/L) did not cause an increase in mortality of the fish. This concentration level was ten thousands times higher than median concentrations often found in this study in particular and in the literature in general. It was aslo thousand times higher than maximum PFOA concentration found in most of survey areas in this study except for Ai River (Yodo River system) in Japan (concentration up to 0.04 mg/L (**V.3.1.1**)). Therefore, concentrations measured in this study might not cause increase in mortality of fathead minnow in water environment. However, it was reported that levels of testosterone hormones were significantly reduced in male and female fish at concentration 1 mg/L, which is just 25 times higher than the concentration measured in Ai River of 0.04 mg/L. Therefore, some adverse effects on fathead minnow might be expected from the contamination of PFOA in surface water.

In another hand, a study conducted on the toxicity of PFOA on zooplankton communities set up in the laboratory (Sanderson *et al.* 2003) showed that the introduction of PFOA at concentrations of 10 mg/l caused the structure of the ecosystem to change. The study suggested that further investigations needed to be carried out to test environmentally relevant concentrations of PFOA on freshwater ecosystems.

V.3.4 Concentrations in WWTP discharges

V.3.4.1 Summary of concentration in WWTP discharges

PFOS and PFOA concentrations in WWTP discharge are summarized in **Table 5.5**. PFOS were detected in all collected samples with an exception of a sample in Istanbul while PFOA were detected in all collected samples well above detection limits. Overall, highest concentration of PFOS were found in Singapore samples, at 467 ng/L in SG-W1, then at 210 ng/L in SG-W4. Those values were at least twice of maximum values found in Yodo

River basin which found at 76.4 ng/L in YO-W3. Differently for PFOA, highest concentrations of PFOA were found in Yodo River samples, at 8000 ng/L, 922 ng/L, and 869 ng/L in YO-W9, YO-W1(1), and YO-W3 respectively followed by samples in Singapore - at 432 ng/L in SG-W5(1).

Table 5.5 Summary of concentrations in WWTP discharges

Survey Area	N	Min	Max	Median	Mean	STD
PFOS						
Yodo River	10	2.5	76.4	8.5	19.8	23.3
Singapore	10	4.6	467.0	23.1	82.6	148.5
Orebro	2	2.5	4.6	3.5	3.5	1.5
Shenzhen	1	-	-	37.6	37.6	-
Istanbul	1	-	-	ND	ND	-
PFOA						
Yodo River	10	25.4	8007.0	47.8	1007.6	2485.0
Singapore	10	9.6	432.4	43.4	90.0	128.3
Orebro	2	2.3	3.1	2.7	2.7	0.6
Shenzhen	1	-	-	29.1	29.1	-
Istanbul	1	-	-	17.0	17.0	-

Several samples collected in WWTPs discharges of the other areas showed relatively lower concentrations of PFOS and PFOA compared with high values in Yodo River and Singapore. Among them, a WWTP in Shenzhen have concentration of both PFOS and PFOA in were relatively higher than those in Orebro and Istanbul (several times higher). Even though it is smaller than median and geomean values in Singapore and Yodo River, those concentrations (37.6 ng/L PFOS and 29.9 ng/L PFOA) were several times higher than minimum values in Yodo River and Singapore River.

V.3.4.2 WWTP discharges versus surface water

Figure 5.23 shows distribution of PFOS and PFOA concentrations in WWTP discharges and those in surface water in individual sampling areas. Concentration in WWTP discharges distributed in the relatively high ranges of concentration often found in surface water with an exception of Istanbul samples for PFOA. In many cases, concentration in WWTP discharges much higher than maximum values found in surface water. It is suggested that WWTP discharge is a source of both PFOS and PFOA in many areas.

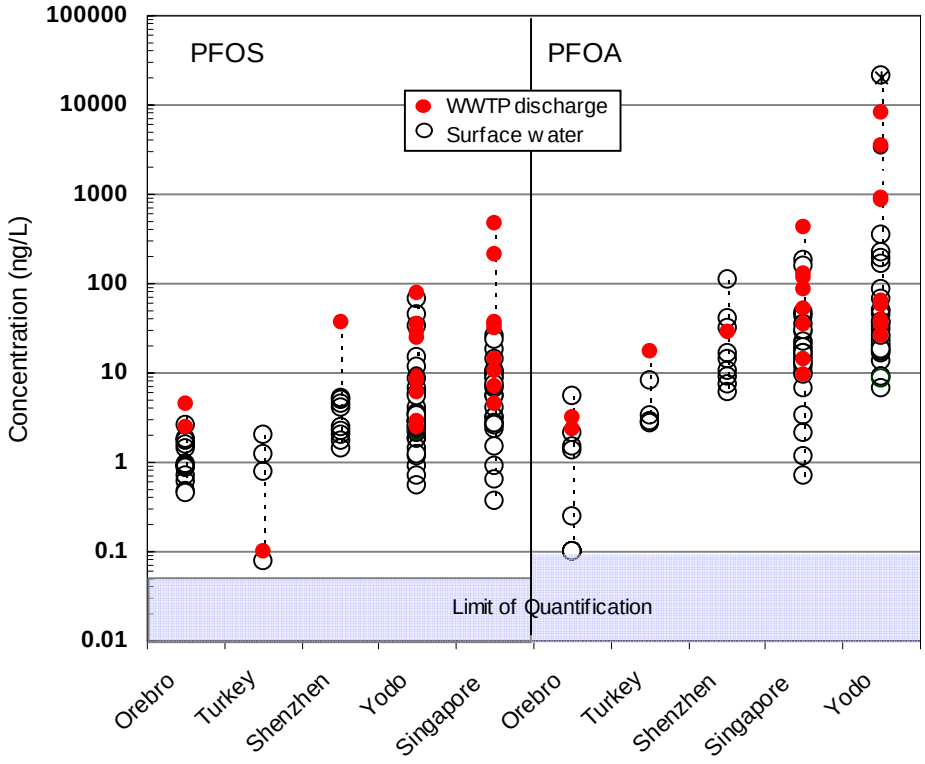

Figure 5.23 PFOS and PFOA concentration in WWTP discharge and in surface water

V.3.5 Relationships between PFOS and PFOA and between PFOS (PFOA) and other parameters

V.3.5.1 PFOS/PFOA ratio

Ratio of PFOS concentration to PFOA concentration (PFOS/PFOA ratio) reflect different pattern of PFOS and PFOA contamination regardless concentration levels. The PFOS/PFOA ratio at individual sampling location were calculated. A summary of PFOS/PFOA ratio in individual sampling areas are shown in **Table 5.6** while the distribution are shown in **Figure 5.24**.

From Figure 5.24, firstly it is observed that the ratios of PFOS concentration to PFOA concentration (PFOS/PFOA ratio) of individual sampling locations often fall in the range of 0.01-1.00. This observation was found in 153 over 185 points, accounting for 83% of total sampling locations. PFOS/PFOA ratio of less than one implies that PFOA concentration were often higher than PFOS concentration regardless of the concentration levels. The finding that PFOA concentration often higher than PFOS concentrations were

in agreement with several study in literatures such as in Nordic Europe (Berger *et al.* 2004) in USA (Sinclair *et al.* 2004, Sinclair *et al.* 2006) for surface water as well as in oceanic waters (Yamashita *et al.* 2005). In addition, the difference between PFOS and PFOA concentration were not higher than two orders of magnitude as shown in the figure with some exception points in Yodo River system (Japan).

Table 5.6 Statistic summary of PFOS/PFOA ratio

Sampling area			N	Min	Max	Median	GM	Mean	STD
1	YO	**Yodo River**	34	**0.001**	0.392	**0.092**	0.070	0.121	0.017
2	KI	Kinki	19	0.076	2.895	0.602	0.362	0.583	0.142
3	SH	Shenzhen	9	0.013	0.452	0.274	0.164	0.229	0.045
4	HN	Hanoi	12	0.019	0.688	0.166	0.134	0.222	0.058
5	PH	Phong River	29	0.017	4.671	0.253	0.256	0.550	0.185
6	CH	Chao Phraya R.	15	0.012	1.929	0.322	0.279	0.429	0.116
7	KK	**Kota Kinabalu**	21	0.184	**40.015**	0.594	1.197	5.091	2.362
8	JB	Johor Bahru	6	0.061	2.193	0.523	0.390	0.898	0.399
9	SG	Singapore	24	0.017	4.953	0.326	0.300	0.650	0.208
10	OR	**Orebro**	12	0.128	**17.800**	**5.500**	3.360	5.911	1.454
11	TR	Turkey	4	0.027	0.736	0.231	0.163	0.307	0.161

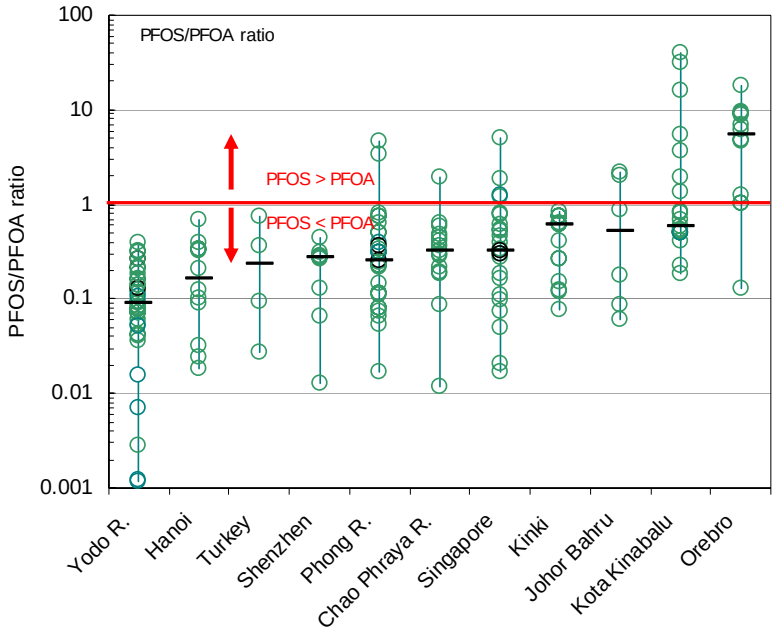

Figure 5.24 Distribution of PFOS/PFOA ratio

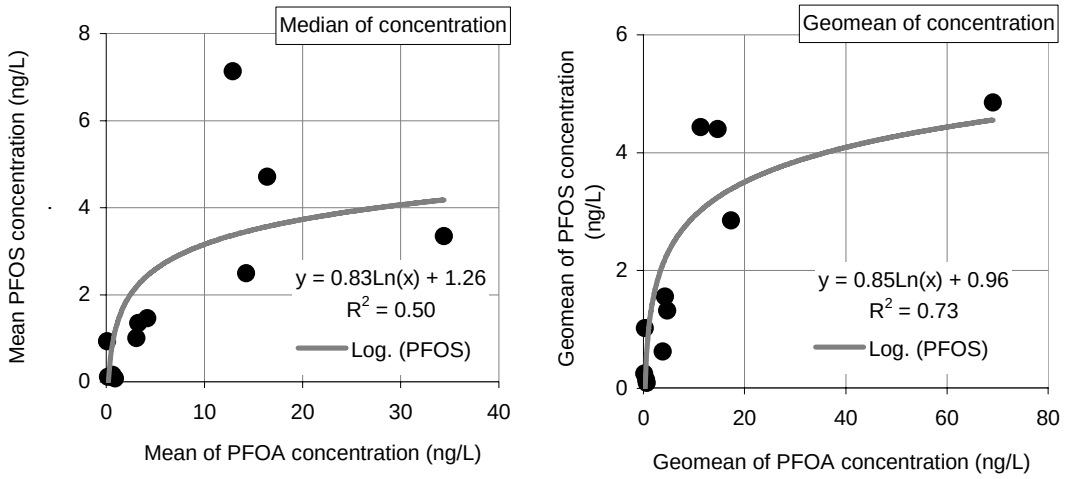

Figure 5.25 Relationship of PFOS concentration (ng/L) and PFOA concentration (ng/L) in terms of median and geometric mean of concentration from different sampling areas

Difference in PFOS/PFOA ratio reflects different patterns of contamination between PFOS and PFOA. Ratio of PFOS/PFOA fluctuated mainly in the range of 0.1-1. Stable PFOS/PFOA ratio means PFOS and PFOA often co-exist. This is supported by log linear relationships between PFOS and PFOA in terms of either geometric mean or median concentration of individual sampling areas. The relationship are shown in **Figure 5.25** with R^2 equal to 0.5 and 0.7 respectively. While significant correlations were observed for average values of individual sampling areas, it was rarely observed for individual sampling locations in each sampling areas (data not shown).

Looking at individual sampling locations, an important point could be seen from Figure 5.24 is that while most of survey areas, PFOS/PFOA ratio fluctuated in the narrow range, the ratio was very small (down to 0.001) for several samples in Yodo river system and was very high (up to several tens) in Kota Kinabalu and Orebro. However, it is important to note that there is uncertainty related with the cases of Orebro, Kota Kinabalu because assumption made on non-dateable level of concentration (concentration were assumed as half of limit of detections for all calculations). As discussed earlier**,** approximately , 30% and 50% were not detected in Kota Kinabalu with PFOS and PFOA respectively and 60% for PFOS in Orebro.

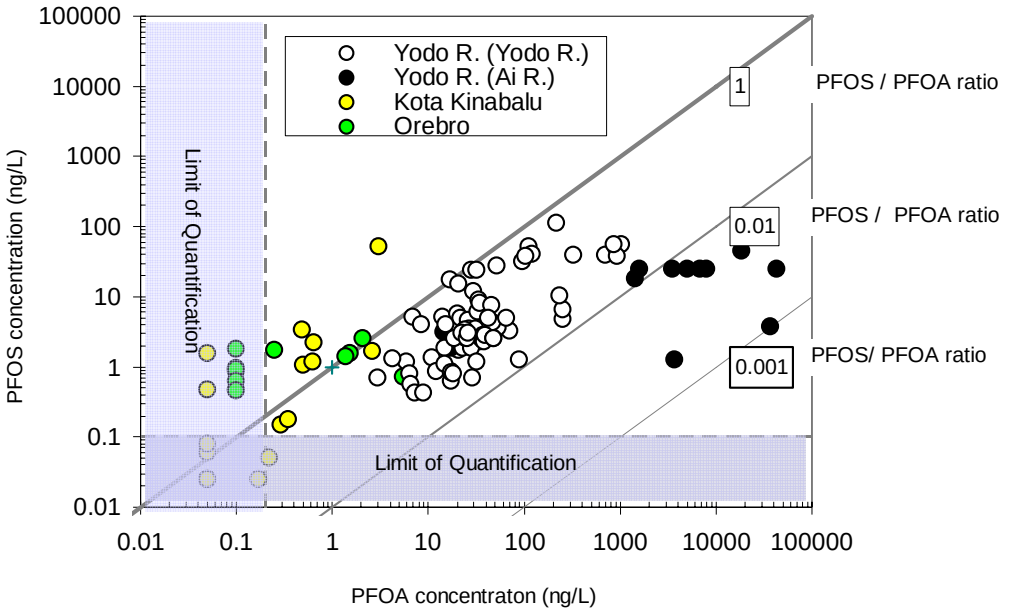

Figure 5.26 PFOS concentration versus PFOA concentration in Yodo River, Kota Kinabalu, and Orebro

In **Figure 5.26**, concentration of PFOS and PFOA in Yodo River, Orebro and Kota Kinabalu were plotted versus each other's In Yodo River system, while an increasing trend of observed for relationship of PFOS to PFOA in most of surface water in upstream of Yodo River with PFOS/PFOA ratio fluctuated in 0.01-1, very low PFOS/PFOA ratio found only in Ai River (an River downstream of the Yodo River system). Low ratio found with with high levels of µg/L order of PFOA concentration indicating a separated point sources of PFOA in this river.

V.3.5.2 Correlation of PFOS (PFOA) with DOC and chloride

Concentration of both PFOS and PFOA were relatively high in Yodo River. Relationships of PFOS (PFOA) with DOC, and with chloride in Yodo River are shown in **Figure 5.27**. In the graph for DOC, PFOS (PFOA) concentrations were expressed as carbon contents. DOC equivalent of PFOS (PFOA) was generally 5 (3) magnitudes order lower than DOC showing that carbon content of PFOS and PFOA accounted for very small fraction of DOC. In addition, contamination profiles of PFOS and PFOA were different from DOC, especially for WWTPs discharges (linear $R^2 < 0.1$). That means higher concentrations of either PFOS or PFOA were not always accompanied with higher DOC concentrations. The

profiles of PFOS and PFOA were also different from that of chloride, which can be considered as an indicator of human activities (linear R^2 < 0.12 for both river sites and WWTP discharges). It suggests that domestic activities alone could not cause the contamination of PFOS and PFOA. There could be little relation between contamination of PFOS and PFOA in the basin with population nor nature.

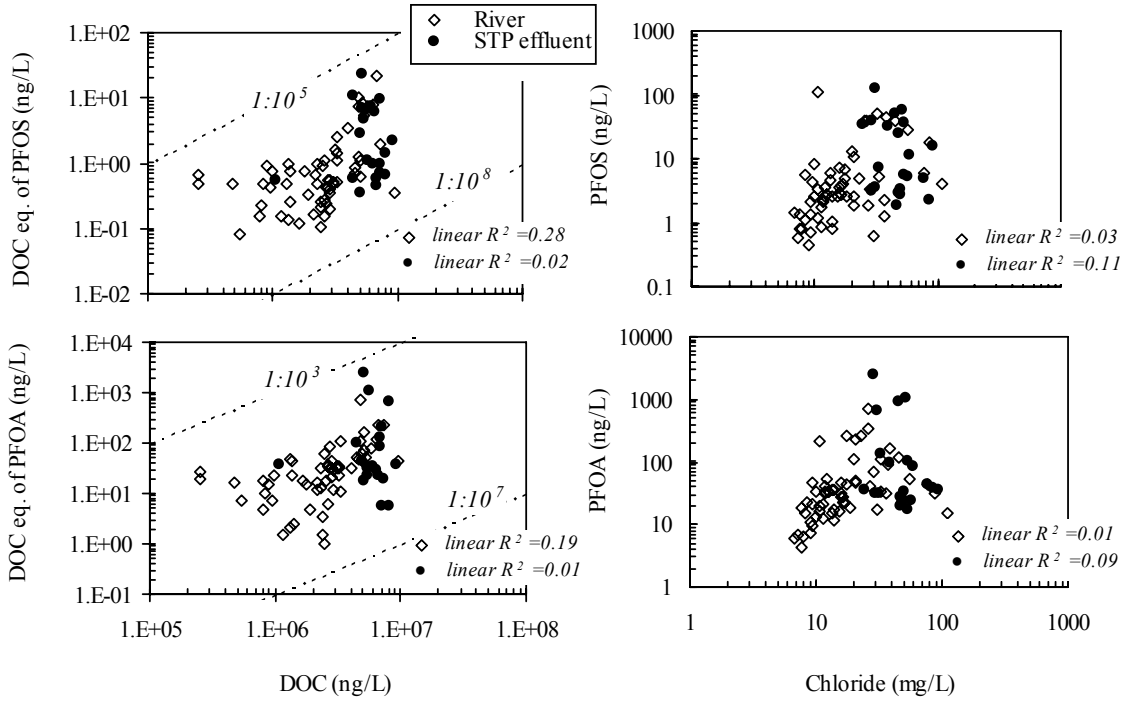

Figure 5.27 Correlations of PFOS (PFOA) with DOC (left), and with chloride (right)

V.4 SUMMARY

Surface water concentrations of PFOS and PFOA have not been reported in many countries including China, Vietnam, Thailand, Malaysia, Singapore, and Turkey. Therefore, there is a strong need to investigate their contamination in those countries in order to know the contamination levels as well as to understand behavior of PFOS and PFOA in surface water environment.

The aims of this chapter are to report concentration of PFOS and PFOA in water environment of certain areas and to discuss about them. Surface water samplings were conducted in Kinki (Japan) (*N*=15), Shenzhen (China) (*N*=9), Hanoi (Vietnam) (*N*=12), Phong River (Thailand) (*N*=29), Chao Phraya River (Thailand) (*N*=15), Kota Kinabalu

(Malaysia) (*N*=21), Johor Bahru (Malaysia) (*N*=6), Singapore (*N*=24), Orebro (Sweden) (*N*=12), and Turkey (*N*=5) (*N* indicates number of sampling locations). Sampling of WWTP discharges were conducted in Yodo River (Japan) (*N*=10), Shenzhen (China) (*N*=1), Singapore (*N*=10), Orebro (Sweden) (*N*=2) and Turkey (*N*=1) (*N* indicates number of sampling locations). Conclusions were as follows.

V.4.1 Concentrations in surface water

1) Overall 90% and 85% of sampling locations (*N*=185) had surface water concentration above detection limits for PFOS and PFOA respectively. Average concentrations at individual sampling locations varied from <0.05 ng/L to 67 ng/L for PFOS and < 0.1ng/L to 21,600 ng/L PFOA. Median of concentrations in individual survey areas ranged from 0.08 ng/L in Hanoi to 7.1 ng/L in Johor Barhu for PFOS and from 0.1 ng/L in Orebro to 34.4 ng/L in Yodo River for PFOA. This reflects ubiquitous pollution of PFOS and PFOA in surface water environment at ng/L order of concentration.

2) Medians (ranges) of PFOS concentrations in individual areas are ranked as follows: Johor Barhu: 7.3 (0.9-26.1), Singapore: 4.7 (0.4-26.5), Yodo River: 3.4 (0.6-67.4), Shenzhen: 2.5 (1.4-5.2), Kinki 1.4 (0.3-13.2), Chao Phraya River: 1.5 (0.2-2.2), Turkey: 1.0 (0.08-2.15), Orebro: 0.93 (0.5-26), Phong River: 0.16 (ND-0.61), Kota Kinabalu: 0.12 (ND-27.8), Hanoi: 0.08 (ND-1.3). Medians (ranges) of PFOA concentrations are ranked as follows: Yodo River: 34.4 (6.6 - 21,600); Singapore 16.4 (0.7-184); Shenzhen: 14.3 (6.1-109.2); Johor Bahru: 12.9 (5.10-18.9); Kinki: 3.3 (0.4-30.0); Chao Phraya River: 4.2 (1.1-20.4); Turkey: 3.1 (2.8-8.1); Hanoi: 0.91 (ND-6.6); Phong River: 0.66 (ND-4.5); Kota Kinabalu: 0.19 (ND-3.22); Orebro: 0.1 (ND-5.53).

3) Repeated samplings were conducted in Yodo River, Phong River and Kota Kinabalu. Concentrations were significantly reproducible among different sampling dates especially in Yodo River where relatively high concentrations of both PFOS and PFOA were observed (CV of less than 0.3 and 0.5 for 50% and 85 % of sampling locations for PFOA and 40% and 70% for PFOS respectively). The results confirm low contamination levels in Phong River and Kota Kinabalu and high concentration levels in Yodo River.

4) High concentration levels were often found in surface water of urbanized and industrialized areas such as Yodo River, Shenzhen, Johor Barhu, Singapore with median concentrations higher than 2 ng/L for PFOS and 10 ng/L for PFOA. Differences in concentration levels were observed among survey areas within a country, as demonstrated

by the cases of Yodo River and other rivers of Kinki in Japan, Chao Phraya River and Phong River in Thailand, and Johor Bahru and Kota Kinabalu. High concentration levels found in this study were comparable with reported values in the USA while low concentration levels were higher than concentration reported in oceanic water suggesting affect of human activities.

V.4.2 Concentrations in WWTP discharges

5) PFOS and PFOA were detected in all WWTP discharge samples with an exception of a sample in Istanbul. Maximum concentration was measured at several hundred ng/L PFOS and thousand ng/L for PFOA in Yodo River and Singapore. The medians (ranges) of concentrations (ng/L) in Yodo River (N=10) were 8.5 (2.5 - 76.4) for PFOS and 47.8 (32.3 - 8,000) for PFOA. Those in Singapore were 23.1 (4.6 - 467) for PFOS and 43.4 (9.57 - 432.5) for PFOA. Several WWTP samples collected in Shenzhen, Orebro, Istanbul have concentration several to several ng/L.

6) Within a survey area, concentrations in WWTP discharges were often higher than those in surface water. It is suggested that WWTP discharges might be sources of PFOS and PFOA in many areas.

V.4.3 Correlation among different parameters

7) PFOS concentration was typically lower than PFOA concentration. Ratio of PFOS concentration to PFOA concentration (PFOS/PFOA ratio) fluctuated in the range of 0.01-1 (observed for 85% sampling locations) suggesting PFOS and PFOA often co-existed. This is supported by log-linear increasing trend of geometric mean of PFOA concentration versus that of PFOA (R= 0.85).

8) In Yodo River, ratio of PFOS/PFOA ratio fluctuated around 0.1 in Yodo River but when down to 0.001 repeatedly in Ai River, where surface water concentration of PFOA were repeatedly measured at several μg/L, indicating a separated point source of PFOA.

9) In Yodo River, profiles of both PFOS and PFOA were different from those chloride and DOC indicating that there could be little relation between contamination of PFOS and PFOA in the basin with population and nature.

CHAPTER VI

CONTAMINATION IN TAP WATERS AND RELATIONSHIP TO SURFACE WATERS

VI.1 INTRODUCTION

Concentration of PFOS and PFOA in tap water were rarely reported. A review has been shown in **Chapter II**. Particularly, before this research was conducted in 2004, some data were available on drinking water contamination with PFOS and PFOA from the USA and Japan (Harada *et al.* 2003, Saito *et al.* 2004) with certain pieces of data (**Table 6.1**). No data on drinking water of Europe and Asia were available in the literature. Recently, Skutlarek *et al.* 2006, by measuring concentrations in tap water and surface water concentration in an area of Germany, indicated that perfluorinated surfactants are at present not successfully removed by water treatment steps.

Table 6.1 Data available on PFOS and PFOA concentration in tap water before 2005

Reference	Prefecture	City	PFOS	PFOA
Harada *et al.* 2003	Iwate	Miyako	•	
Harada *et al.* 2003	Tokyo	Setagaya	•	
Harada *et al.* 2003		Morioka	•	•
Harada *et al.*2003, Saito *et al.* 2004,	Kyoto	Kyoto	•	•
Saito *et al.* 2004	Hyogo	Hanshin	•	•
Saito *et al.* 2004	Osaka	Osaka	•	•
Saito *et al.* 2004	Iwate	Morioka	•	•
Saito *et al.* 2004	Miyagi	Sendai	•	•
Saito *et al.* 2004	Akita	Yokote	•	•

Human exposure pathways of PFOS and PFOA were not discussed in the literatures. PFOS and PFOA, if present in drinking water, will pose a risk of human exposure through drinking pathway. Harada *et al.* 2003 reported that contamination in drinking water (about 50 ng/L PFOS) near Tama River (Japan) could result in extra 25-50% rise of the average serum concentration from the average value of 28.4 ng/L as reported by Hansen *et al.* (2002). PFOS and PFOA have long half-life in human body (8.67 and 1-3.5 years for PFOS and PFOA respectively as reported by Hekster *et al.* 2003). They are accumulation in blood of not only occupationally exposed workers but also general population of various countries.

This chapter has two objectives. Firstly, it is to report for the first time tap water concentration from various locations of several countries. Secondly, it is to find out weather there were any relation between tap water concentrations and surrounding surface water concentrations (data reported in **Chapter V**), which can or cannot be the sources of tap water supply.

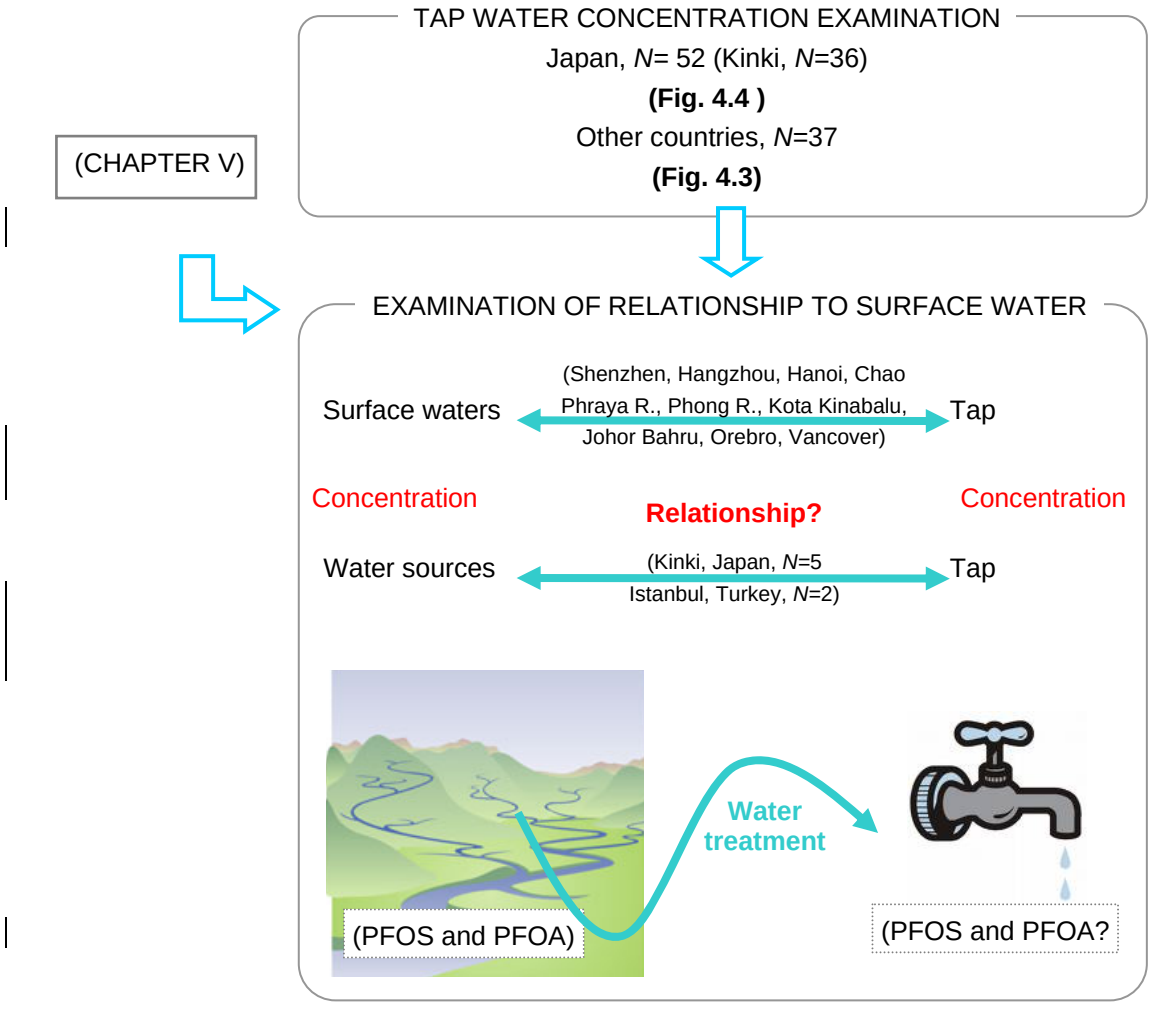

Figure 6.1 An inlustration of Chapter VI contents

VI.2 MATERIALS AND METHODS

VI.2.1 Sampling and water analysis

Sampling of tap water were conducted by two schemes: collection of tap water in the same environmental water survey areas and spot collection of for other locations. In addition a

tap water contamination survey were conducted in Kinki, Japan. Details of sampling and analysis has been described in Chapter IV. **Table 6.2** summaries tap water sampling locations and corresponding surface water.

Table 6.2 A summary of tap water sampling locations and number of samples

Country	Tap water		Corresponding surface water	
	Sampling area	Sample number	Sampling area	Note
Japan	Kinki	**36**	Kinki	
	Others	**16**	-	Not available
China	Shenzhen	**5**	Shenzhen	
	Hangzhou	**1**	Hangzhou	Spot sampling
	Kunming	**1**	Kunming	Spot sampling
Vietnam	Hanoi	**2**	Hanoi	
Thailand	Bangkok,	**7**	Chao Praya River	
	Khon Kaen	**3**	Phong River	
Malaysia	Kota Kinabalu	**4**	Kota Kinabalu	
	Johor Bahru	**2**	Johor Bahru	
	Penang, Kuala Lumpur	**3**	-	Not available
Turkey	Istanbul	**4**	Istanbul	Spot sampling
	Newsehir	**1**	Newsehri	Spot sampling
Sweden	Orebro	**2**	Orebro	
Canada	Vancouver	**1**	Vancover	Spot sampling
	Calgary	**1**	-	Not available
Total		**89**		

VI.2.2 Data analysis

Median and standard deviations were calculated. When indicated, the geometric mean (GM) and geometric standard deviation (GSD) were calculated. Values of less than (LOQ) are assumed as half of (LOQ) values for calculations as well as for graph display. Data analysis also use *t*-test which applies analysis of two samples assuming unequal variances, α=0.05. When $p<0.05$, the difference is considered to be significant.

Results of tap water concentration will be shown in three parts: (1) tap water in Kinki Japan, (2) tap water from other locations in Japan and (3) tap water from other countries.

VI.3 RESULTS AND DISCUSSION

VI.3.1 Tap water concentration in Japan

VI.3.1.1 Kinki Region

Tap water concentrations in Kinki Region are shown in **Table 6.3** together with available data in literature for comparison. Except for one sample that was not detected with PFOS, all 36 tap water samples collected in Kinki regions show detectable levels of PFOS and PFOA. Highest concentrations were measured at 8.6 ng/L PFOS in a sample collected in Moriguchi City and at 42.3 ng/L for PFOA in a sample collected in Matsubara city. Both cities were within Osaka Prefecture where Yodo River is water supply sources. Tap water concentrations were found relatively high in samples collected in other cities in Osaka Prefecture. For examples in Takatsuki repeatedly sampling were conducted at the same location (T-JP36, 37, 38, 39) showed average concentration of 2.9 ± 1.8 ng/L PFOS and 31.8 ± 9 ng/L PFOA (*N*=4).

Tap water concentration fluctuated in samples collected from different cities in Kyoto Prefecture. Concentration in Kyoto City ranged 1-2 ng/L PFOS and 4.2-15.9 ng/L PFOA.

Table 6.3 Tap water concentrations in Kinki region (Japan) (* and ** indicated water sourced from Lake Biwa and Yodo River respectively)

Code		Prefecture	City	Town	Sampling date	PFOS (ng/L)	PFOA (ng/L)	Note
T-JP	17	Hyogo	Himeji		2006-12-23	0.86	1.4	
T-JP	18	Hyogo	Kakogawa		2006-12-23	2.75	4.1	
T-JP	19	Hyogo	Kawanishi		2006-12-23	1.51	1.91	
T-JP	20	Hyogo	Kobe	Arima	2006-08-16	7.08	8.38	**
T-JP	21	Hyogo	Kobe		2006-12-23	1.94	7.89	**
T-JP	22	Hyogo	Nishinomiya	Hagoromo-cho	2005-08-01	ND	0.34	
T-JP	23	Hyogo	Sasayama		2006-12-23	9.13	7.29	
T-JP	24	Kyoto	Kyotamba		2006-12-27	0.2	0.35	
T-JP	25	Kyoto	Kyoto	Sakyo	2005-08-01	0.93	6.74	*
T-JP	26	Kyoto	Kyoto	Yamashina	2007-01-03	0.95	4.2	*
T-JP	27	Kyoto	Kyoto	Yamashina	2006-05-12	2.03	15.19	*
T-JP	28	Kyoto	Maizuru		2006-12-27	0.39	4.79	

Note: to be continued

Table 6.3 Tap water concentrations in Kinki region (Japan) (continued)

Code		Prefecture	City	Town	Sampling date	PFOS (ng/L)	PFOA (ng/L)	Note
T-JP	29	Kyoto	Miyazu		2006-12-27	0.06	0.37	
T-JP	30	Kyoto	Uji		2006-12-31	1.23	7.53	*
Saito et al. 2004		*Kyoto*	*Kyoto*	-	*2003-04-21*	*4.90*	*5.40*	
T-JP	31	Nara	YamatoKoriyama	Takada-cho	2006-12-19	0.38	1.34	
T-JP	32	Nara	YamatoKoriyama	Takada-cho	2005-08-01	0.06	1.29	
T-JP	33	Osaka	Kansai Airport		2006-11-20	2.74	16.95	
T-JP	34	Osaka	Matsubara		2006-12-19	2.01	42.35	**
T-JP	35	Osaka	Moriguchi	Toyohide-cho	2006-08-03	8.46	25.37	**
T-JP	36	Osaka	Takatsuki	Seifukuji-cho	2006-07-20	5.59	18.32	**
T-JP	37	Osaka	Takatsuki	Seifukuji-cho	2005-08-01	1.92	34.33	**
T-JP	38	Osaka	Takatsuki	Seifukuji-cho	2006-05-11	1.97	37.05	**
T-JP	39	Osaka	Takatsuki	Seifukuji-cho	2006-05-19	1.9	37.53	**
T-JP	40	Osaka	Takatsuki	South part	2006-08-06	3.27	6.59	**
T-JP	41	Osaka	Toyonaka	Terauchi-cho	2006-09-17	2.54	24.33	**
T-JP	42	Osaka	Toyonaka		2006-12-23	5.67	8.17	**
Saito et al. 2004		*Oskaka*	*Osaka*	-	*2003.4.12*	*12.0*	*40.0*	
T-JP	43	Shiga	Hikone		2006-12-13	1.31	6.46	*
T-JP	44	Shiga	Otsu	Ogoto	2006-12-13	1.4	6.4	*
T-JP	45	Shiga	Otsu	Yumihama	2006-12-13	0.82	7.01	*
T-JP	46	Shiga	Otsu	Yumihama	2006-05-16	2.52	13.93	*
T-JP	47	Shiga	Otsu	Yumihama	2005-07-01	1.54	8.31	*
T-JP	48	Shiga	Otsu	Yumihama	2005-07-01	0.81	5.8	*
T-JP	49	Shiga	Takashima	Adogawa	2006-12-13	0.21	0.85	
T-JP	50	Shiga	Takashima	Shinasahi	2006-12-13	0.07	0.64	
T-JP	51	Wakayama	Hashimoto		2006-01-03	1.96	1.21	
T-JP	52	Wakayama	Wakayama		2006-12-19	1.92	3.24	

Comparable levels were found in Uji City at 1.2 ng/L and 7.5 ng/L respectively while lower concentrations were found in Kyotamba City at 0.2 ng/L and 0.35 ng/L. Kyoto and Uji city have water source from Lake Biwa, Kyotamba city have water sources from upstream of Yura River.

In Shiga Prefecture, similar levels of PFOS and PFOA to those of Kyoto and Uji City was found, at 0.8-2.5 ng/L PFOS and 5.8-13.9 ng/L in Otsu (Yumihama, Ogoto) and Hikone. Repeated sampling in Yumihama (*N*=4) confirm the contamination levels (CV=0.6 for PFOS and 0.4 for PFOA). Similar levels of concentration in Otsu and Hikone with those of Uji and Kyoto is probably due to same water supply source, which is Biwa Lake. On the other hand, concentrations in Takashima city (Adogawa and Shinasasshi) have significantly lower concentration of PFOS (0.07-0.21 ng/L) as well as PFOA (0.64-0.85 ng/L). That might be due to the fact that Lake Biwa does not supply water for Takashima City at the areas where sampling location located.

Tap water sample collected from various location in Hyogo Prefecture also significantly fluctuated. Lowest levels, at ND PFOS and 0.34 ng/L PFOA, was found in Nishinomiya, while other samples collected fluctuated in 0.86-9.13 ng/L PFOS and 1.4-8.38 ng/L PFOA. Tap water in Kobe city have water supply partly from Yodo River while Nishinomiya tap water source is completely not Yodo River water.

Relatively low concentrations were found in samples collected in Wakayama and Nara Prefectures. Sample collected in YamatoKoriyama, Nara prefecture was found repeatedly at low level (0.06-0.38 ng/L PFOS and 1.29-1.34 ng/L for PFOA). Water source of this city is ground water. The city of Hashimoto and Wakayama in Wakayama Prefecture have concentration of 1.96-1.92 ng/L PFOS and 1.21 and 1.34 ng/L PFOA. Both cities have water supply from Kino River.

VI.3.1.2 Other locations in Japan

Table 6.4 shows concentrations of tap water samples collected outsides Kinki region. It also showed detectable levels of PFOS and PFOA with only one samples collected in Miyazaki that was not detected with PFOA. PFOS and PFOA concentration were relatively high in two samples collected in Tokyo at 2.7-7.7 ng/L PFOS and 6.7-15 ng/L PFOA which were comparable to those of Kyoto. It has been reported relatively high levels of PFOS and PFOA in Tokyo at two values of 2.4-4.0 ng/L and 44-51 ng/L respectively at two locations of Setagaya city (Harada *et al.* 2003). A sample collected in Okayama also

Table 6.4 PFOS and PFOA concentration in Japanese locations beyond Kinki region

Sample identification					Concentration (ng/L)	
CODE	**Prefecture**	**City**		**Sampling date**	**PFOS**	**PFOA**
T-JP 1	Hokkaido	Kamikawa	Furano	2006-09-02	2.17	1.91
T-JP 2	Hokkaido	Oshima	Hakodate	2006-11-20	0.24	0.42
T-JP 3	Hokkaido	Oshima	Hakodate	2006-11-20	0.18	0.51
T-JP 4	Hokkaido	Ishikari	Sapporo	2005-08-01	0.05	0.61
T-JP 5	Miyagi	Sendai	Sakunami	2006-07-31	0.07	0.59
T-JP 6	Miyagi	Sendai	Taihaku-ku	2006-03-16	0.39	1.22
Harada et al. 2003	*Miyagi*	*Sendai*	-	*2003-04-18*	*0.10*	*0.13*
T-JP 7	Yamagata	Yamagata	Zao	2006-03-18	0.58	1.08
T-JP 8	Tokyo	Ikebukuro	-	2006-07-05	7.74	15.09
T-JP 9	Tokyo	Chiyoda	-	2006-05-18	2.68	6.68
Harada et al. 2003	*Tokyo*	-	-	-	*2.4-4.0*	-
Harada et al. 2003	*Tokyo*	-	-	-	*43.7-51.0*	-
T-JP 10	Kanagawa	Yokohama	Honmoku-cho	2006-09-03	0.72	2.45
T-JP 11	Ishikawa	Kanazawa	-	2006-12-19	0.10	0.35
T-JP 12	Tottori	Tottori	Tomiyasu-cho	2005-11-01	0.11	0.66
T-JP 13	Okayama	Kurashiki	Ohama Coast	2005-10-30	0.60	4.20
T-JP 14	Okayama	Okayama	Marunouchi	2005-10-31	0.10	7.50
T-JP 15	Kagawa	Nakatado-gun	Kotohira-cho	2005-10-29	6.80	3.10
T-JP 16	Miyazaki	Miyazaki	Yamasaki-cho	2006-10-01	0.28	ND

show relatively high concentrations of PFOA and a sample collected in Kagawa showed relatively high concentration of both PFOS and PFOA. Concentration in other locations (N=11) fluctuated 0.07-2.17 ng/L PFOS and 0.35-2.45 ng/L PFOA, significantly lower than those in samples collected in Osaka Prefectures. Tap water samples collected from Sendai had 0.07-0.39 ng/L PFOS and 0.59-1.22 ng/L PFOA while it was reported average values of 0.1 ng/L PFOS and 0.13 ng/L PFOA (Saito *et al.,* 2004).

VI.3.2 Tap water concentration outside Japan

Tap water concentrations measured from various countries outside Japan are shown in **Table 6.5**. While all collected samples in Japan show detected levels for almost tap water samples 8/37 and 9/37 tap water samples collected from outside Japan were not detected with either PFOS nor PFOA. However, among non-detected samples, many samples were collected from Kota Kinabalu, Hanoi, Khon Kean, where surface water had showed relatively low levels as discussed in **Chapter V**.

Table 6.5 Results of tap water concentration outside Japan

Code	Sampling location identification				Sampling Date	PFOS (ng/L)	PFOA (ng/L)
	Country	State/Province	City	Sub-region			
T- CN1	China	Guangdong	Shenzhen	Nanshan	2005-10-11	6.48	3.10
T- CN2	China	Guangdong	Shenzhen	Luohu	2005-10-11	6.20	2.30
T- CN3	China	Guangdong	Shenzhen	Luohu	2006-01-19	9.92	1.10
T- CN4	China	Guangdong	Shenzhen	Futian.	2006-10-19	10.02	10.12
T- CN5	China	Guangdong	Shenzhen	Nanshan	2006-10-20	4.06	7.75
T- CN6	China	Yunnan	Kunming	-	2005-10-22	13.18	1.08
T- CN7	China	Zhejiang	Hangzhou	-	2006-05-09	1.45	109.34
T- VN1	Vietnam	Hanoi	Hanoi City	Thanh Xuan	2006-01-26	ND	ND
T- VN2	Vietnam	Hanoi	Hanoi City	Thanh Xuan	2006-01-28	ND	ND
T- TL4	Thailand	Bangkok	Bangkok City	-	2005-12-16	1.91	4.63
T- TL5	Thailand	Bangkok	Bangkok City	-	2006-01-11	9.46	1.52
T- TL6	Thailand	Bangkok	Bangkok City	Pratunam	2006-07-17	11.63	5.81
T- TL7	Thailand	Pathumthani	Khlong Luang	-	2006-07-17	6.76	1.45
T- TL8	Thailand	NakhonPathom	Phuttamonthon	-	2006-12-05	0.23	10.01
T- TL9	Thailand	Bangkok	Bangkok City	-	2006-12-05	1.28	2.49
T- TL10	Thailand	Bangkok	Bangkok City	Sukhumvit	2006-12-05	2.18	6.48
T- TL1	Thailand	Khon Kaen	Muang Dist.	-	2005-07-16	0.15	ND
T- TL2	Thailand	Khon Kaen	Muang Dist.	-	2005-07-17	0.24	3.40
T- TL3	Thailand	Khon Kaen	Muang Dist.	-	2006-01-19	0.10	0.21
T- MY5	Malaysia	Johor	Johor Bahru	Kampong Maju Jaya	2006-10-09	0.34	29.2

Note: to be continued

Table 6.5 Results of tap water concentration outside Japan (continued)

Code	Sampling location identification				Sampling Date	PFOS (ng/L)	PFOA (ng/L)
	Country	State/Province	City	Sub-region			
T- MY6	Malaysia	Johor	Johor Bahru	-	2006-10-09	0.23	18.1
T- MY1	Malaysia	Sabah	Kota Kinabalu	Menggatal	2005-08-30	0.08	0.13
T- MY2	Malaysia	Sabah	Kota Kinabalu	-	2005-09-01	ND	ND
T- MY4	Malaysia	Sabah	Kota Kinabalu	-	2005-11-24	ND	ND
T- MY7	Malaysia	Kuala Lumpur	Kuala Lumpur	-	2006-08-29	1.00	2.07
T- MY8	Malaysia	Kuala Lumpur	Kuala Lumpur	-	2006-08-30	0.26	ND
T- MY9	Malaysia	Penang	Penang Island	Batu Ferringhi	2005-11-23	ND	ND
T- SE1	Sweden	Närke	Orebro Municipality	Frovi	2006-03-08	0.33	1.32
T- SE2	Sweden	Närke	Orebro Municipality	Orebro Town	2006-03-09	0.83	ND
T- TR1	Turkey	Istanbul	Istanbul City	-	2006-09-21	0.52	4.43
T- TR2	Turkey	Istanbul	Terkos	-	2006-09-21	0.61	5.21
T- TR3	Turkey	Istanbul	Sazlidere	-	2006-09-21	2.37	3.97
T- TR4	Turkey	Istanbul	Istanbul City	Maslak	2006-09-21	0.33	3.65
T- TR5	Turkey	Newshehir			2006-09-18	0.08	9.80
T- CA2	Canada	Alberta	Calgary		2005-09-14	ND	0.16
T- CA1	Canada	British Columbia	Vancouver		2005-09-11	ND	0.24

Tap water samples collected in China were all detected with PFOS and PFOA. This observation was similar for what observed for surface water samples in Shenzhen. Concentrations in several locations ranged of 4.06-10.02 ng/L PFOS and 1.1-7.75 ng/L PFOA. Maximum PFOS concentration were higher than those for water samples collected which was 4.8 ng/L PFOS. Maximum PFOA concentration were comparable with contamination in water samples collected in Xinzhou River as shown in **Table 5.7.** Other samples collected in China (spot samples in Kunming and Hangzhou) also had relatively high concentration. It is notable exceptionally high concentration of PFOA, measured at 109 ng/L in Hangzhou tap water beyond the PFOA concentration reported in Japan so far.

In Thailand, PFOS and PFOA were found at relatively low concentration in Khon Kaen but relatively high in the Central Provinces of Thailand (Bangkok, Pathumthani, Nakhon Pathom) that within Chao Phraya River sub basin. Concentrations in Bangkok ranged from 1.28-11.63 ng/L PFOS and 1.52-6.48 ng/L PFOA which were comparable with those in Chao Phraya River surface water.

In Malaysia, samples collected from Kota Kinabalu were rarely detected with PFOS and PFOA as shown in **Table 6.3** but it was detected quite high concentration of PFOA in Johor Barhu. PFOA concentrations were at 18.1-29.2 ng/L which were comparable to those found in several surface water in Tebrau River and Skudai River. PFOS concentrations were smaller of less than 1 ng/L and were comparable with those of Skudai. PFOS and PFOA were also found in two tap water samples collected in Kuala Lumpur while a sample collected in Penang was not found with either PFOS or PFOA.

All tap water samples collected in Turkey was detected with PFOS and PFOA. PFOS concentration ranged from 0.08 in a sample collected in Nevsehir to 2.47 ng/L in a sample collected in Istanbul. PFOA concentrations ranged 3.7-9.8 ng/L. The concentration levels were somewhat comparable to those of Kyoto City.

Tap water samples collected in Sweden and Canada showed low level of PFOS and PFOA. Low contamination in Orebro were seemed to be similar to those of surface water. In Canada, PFOS were not detected in Vancouver and Calgary. A lake water sample collected in Vancouver was also measured at low concentration (0.1 ng/L PFOS and 0.8 ng/L PFOA)

VI.3.3 Summary of tap water concentrations

A statistic summary of tap water concentrations are shown in **Table 6.6**. The summary is calculated based on three groups those are Yodo River basin, Japan except for Yodo River basin and other countries.

Overall maximum concentrations for PFOA were found at 42.4 ng/L in Kinki and Japan, at 109.3 ng/L PFOA outside Japan. Those for PFOS were relatively lower, found at 7.7 ng/L in Kinki Region, 9.1 ng/L in Japan and 13.8 ng/L in other countries. Highest PFOS concentration at 13.2 ng/L found in a Kunming sample in fact was lower than concentration levels of tap water found in Tama River, Japan as reported by Harada *et al.* (2003), at about 50 ng/L. Highest PFOA concentration of 109 ng/L, which found in Hangzhou, is less than maximum concentration reported in Rhine-Ruhr area, Germany at

519 ng/L. Even thought the maximum levels higher than those reported in literature was not found, it is important to shows that tap water samples collected from various locations in many countries were contaminated with PFOS and PFOA.

Table 6.6 Statistical summary of tap water concentration

	N	*N*-detected	Min	Max	Median	GM	Mean	CV
PFOS								
Yodo*	15	15	0.93	8.46	2.01	**2.65**	2.96	0.78
Japan**	30	29	0.01	9.13	0.38	**0.48**	1.41	1.67
Other countries	37	29	0.03	13.18	0.34	**0.50**	2.50	1.53
PFOA								
Yodo*	15	15	6.40	42.35	8.38	**11.76**	14.50	0.78
Japan**	30	29	0.03	15.09	1.26	**1.43**	2.52	1.27
Other countries	37	28	0.05	109.34	2.07	**1.13**	6.75	2.71

*Note: * Yodo River basin, **Japan except for Yodo River*

*Note: *Calculated based on sampling locations (Result of sampling location that have repeated sampling average values of different sampling dates).*

Concentration levels of both PFOS and PFOA in Kinki Region were significantly higher than those in other part of Japan, with geomean of concentration of 2.65 ng/L and 0.48 ng/L for PFOS and 11.8 ng/L and 1.43 ng/L for PFOA respectively. The different were quite significant with $p<0.05$ values (t-test) for both PFOS and PFOA.

Concentration of tap water samples collected in Yodo River basin is quite low-variance with CV equal to 0.78 for both PFOS and PFOA. On the other hand, concentrations in various locations in Japan is highly variable (CV of 1.67 and 1.27). Concentrations fluctuated from different locations in a country and from different countries. However, concentration of samples collected in the same area seemed not to be highly fluctuated with CV values less than 1 for most cases (CV not shown).

VI.3.4 Relationship between tap water and surface water contamination

VI.3.4.1 Tap water versus surface water

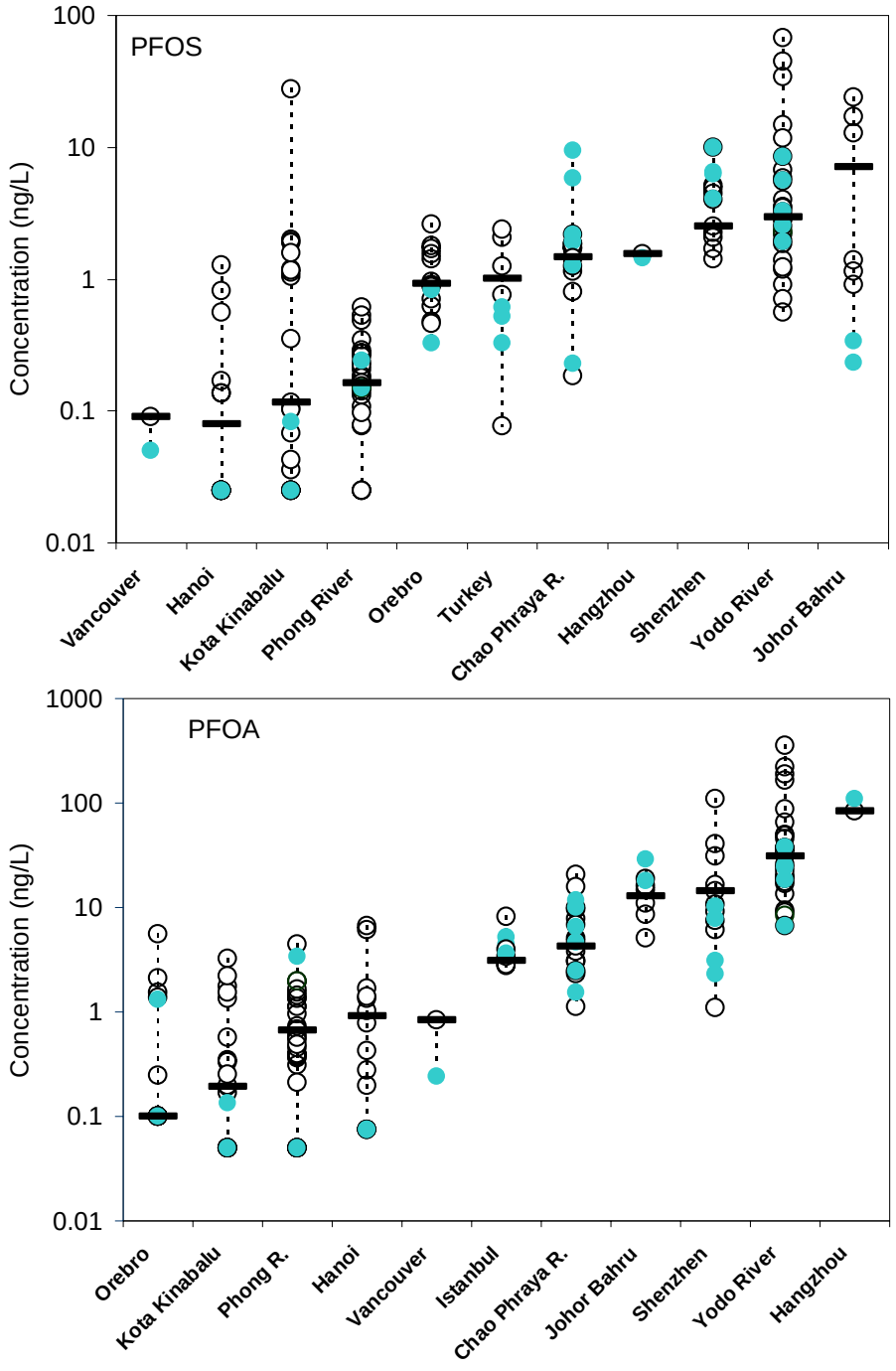

Figure 6.2 Distribution of tap water concentrations versus surface water concentrations

Figure 6.2 shows distribution of PFOS and PFOA concentrations in tap water samples and those in surface water for individual sampling areas (data taken from **Chapter V**).

Concentration in tap water samples often distributed within the ranges of surface water concentration with a few exceptions.

Tap water concentration and surface water from different areas inside and outside Japan are compared. Geometric means of tap water and surface water concentrations in each area are used as representative values and plotted versus each other as shown in **Figure 6.3** for both PFOS and PFOA. The graphs depict increasing trends of tap water level following increasing surface water level. Linear relationship were found at a value of 0.74 and 0.91

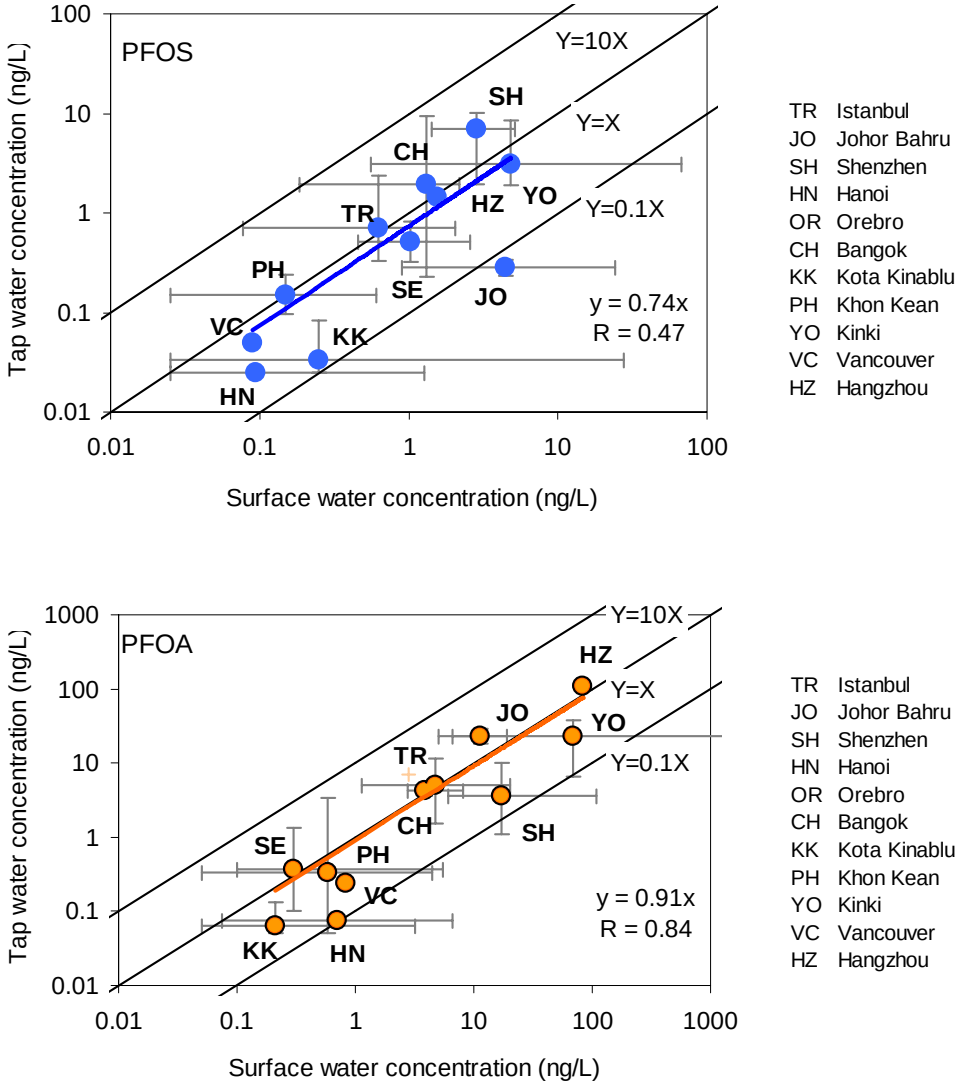

Figure 6.3 Geomean of PFOA concentrations in tap water versus those in surface water

for PFOS and PFOA respectively with corresponding R of 0.47 and 0.84.

For PFOS besides the high levels in Kinki in both water types, levels in Shenzhen were high, and corresponding to those of surface water. For PFOA, concentration in Hangzhou were highest, as stated before, also shows corresponding to concentration of surface water sample (West Lake water) which was found at 84 ng/L. Therefore, further investigation is recommended.

Low tap water contamination in Hanoi, Kota Kinabalu, Khon Kean, and Vancouver seem to be related with the observed concentration in the surface waters. Surface water concentration were also relatively high in Johor at geomean levels of 4.4 ng/L PFOS for surface water but lower in tap water samples collected (0.3 ng/L). Differently PFOA concentrations in tap water were measured at minimum level of 18 ng/L while maximum level of surface water samples found at 19 ng/L. Although, the surrounding surface water of an area might not always be tap water source, the main observation was that the contamination levels in tap were similar to those in surface water.

VI.3.4.2 Tap water versus water sources

As discussed in previous section, in Kinki region, sampling location that have water supply sources beyond Yodo River basin often had significant lower concentration of both PFOS and PFOA compared with those of Yodo River. Thus, contamination of water supply sources might have effect on tap water. A case study was conducted in Kinki region to further search for water sources in order to compare their concentrations with those in tap water samples. **Table 6.7** shows sampling locations of water supply source and corresponding tap water sample location in Kinki Region (Japan). In addition, two cases in Istanbul (Turkey) are also shown in the Table.

Comparison between concentrations in water supply sources and tap water are shown in **Figure 6.4**. It is used concentrations taken from Table 6.3 and Table 6.5 for tap water with average result calculated for repeated sampling or similar water sources. Surface water results can be referred from **Chapter V** with average concentration calculated.

The figures indicates general increasing trend of PFOS concentration in tap water while increasing water source concentration. Similarity was observed for PFOA. For both PFOS and PFOA, surface water reached highest at JP (3) where water sources is Yodo River and tap water locations are in Osaka Prefecture. Average concentrations in tap water and water sources were 4.4 ng/L and 3.1 ng/L for PFOS and 29.6 ng/L and 29.0 for PFOA. It should

be noted that water supply source in Takatsuki City (Seifukuji-cho) of Osaka prefecture passed through ozonation followed by activated carbon step but concentration were repeatedly found at about 2 ng/L PFOS and 30 ng/L PFOA as shown in Table 6.2.

JP (2) is the case where water sources is Lake Biwa, Yodo River upstream. Tap water concentration in supply cities have concentrations of 1.3 ng/L PFOS and 7.6 ng/L PFOA in average, about haft of the case in Yodo River downstream. Those levels of tap water were also comparable to those of Lake Biwa with average concentration of 1.7 ng/L PFOS and 12 ng/L PFOA respectively. Tap water concentrations were smallest at JP (7) for the case of upstream Yura River with concentration in river samples were as small as at 0.27 ng/L PFOS and 0.4 ng/L PFOA but tap water concentration still shows the presence of both chemicals at the comparable levels.

Table 6.7 Sampling location of water sources and corresponding tap water in Kinki Region (Japan) and Istanbul (Turkey)

Water supply sources			**Corresponding tap water**		**Code**
River system	**Name**	**Position**	**Prefecture**	**City**	
Kinki Region (Japan)					
Yodo River	Lake Biwa	(1) Hikone, (2) Otsu, (3) Lake Biwa Cnl.	Shiga, Kyoto	Hikone, Otsu, Kyoto, Uji	JP (2)
Yodo River	Yodo River	(1) Sugawarashirokitao BRG., (2) Kunjima Island, (3) Torikai BRG., (4) Hirakata BRG.	Osaka, Hyogo	Takatsuki, Toyonaka, Moriguchi, Matsubara	JP (3)
Kino River	Kino River	Wakayama	Wakayama	Wakayama	JP (4)
Yura River	Yura River	Kyotamba	Kyoto	Kyotamba	JP (7)
Yura River	Yura River	Maizuru	Kyoto	Maizuru	JP (8)
Ina River	Ina River	Hitokura Dam	Hyogo	Kawanishi	JP (5)
Ichi River	Ichi River	Kotani Dam	Hyogo	Himeji	JP (6)
Kako River	Kako River upstream	(1) Kawashiro Dam, (2) Okawase Dam, (3) Dondo Dam	Hyogo	Kakogawa, Sasayama	
Istanbul (Turkey)					
Terkos Lake		Terkos WSP inflluent	Terkos WSP effluent		TR (1)
Sazlidere Lake		Sazlidere WSP influent	Sazlidere WSP effluent		TR (2)

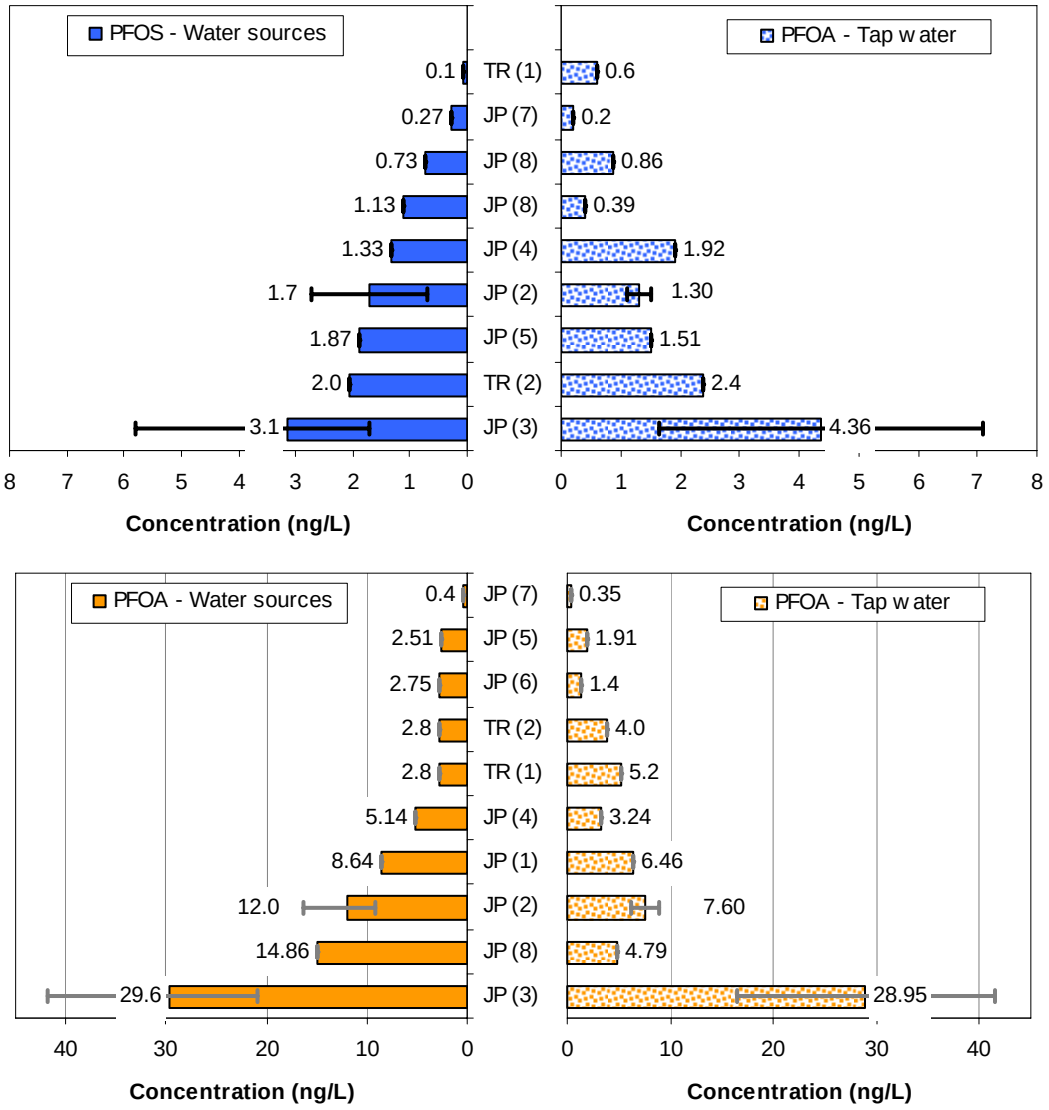

Figure 6.4 Concentrations in tap water and their water source

A big difference for PFOA were found at point JP (8) where water supply source is Yura River downstream and tap water is Maizuru City, with approximately 70% of PFOA concentration reduction. Water treatment step in this city is without advance treatment. Surface water and tap water in were collected in the same day but sampling notes indicated significant rain throughout the Yura River basin for about a day that might increase surface water concentration. The samples in fact are of single samples, therefore, error should not be ruled out. Further investigation is needed.

Tap water samples in Istanbul also shows corresponding to water supply sources. In Istanbul, sampling of tap water were directly conducted at effluents of water supply plants while sampling of water supply source were also directly as influent of those plants on the

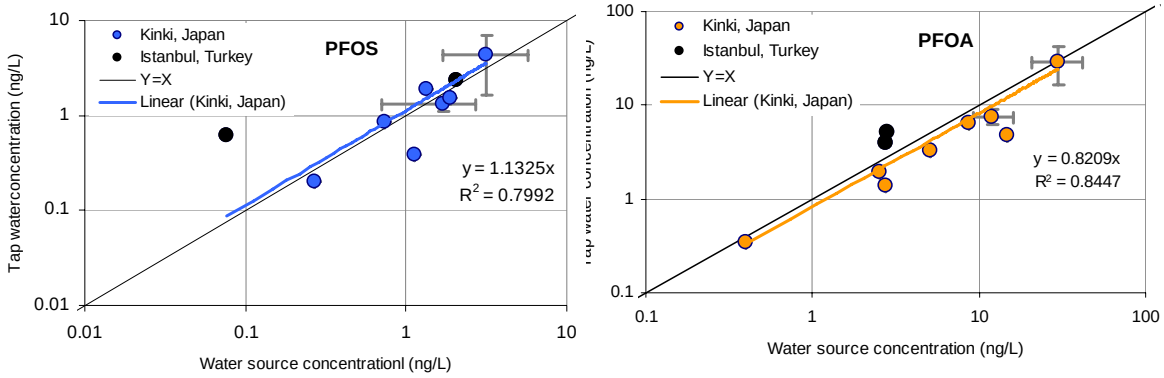

Figure 6.5 Correlation in PFOS concentrations between tap water and water supply sources in Kinki, Japan (Istanbul data show for comparison)

same days. Tap water and surface water concentration of PFOS for TR (2) were higher than those TR (1) and comparable with those in Lake Biwa. Concentration of PFOA for both cases show increasing of concentration through water treatment steps. Further study is needed.

Overall, there is similarity in concentration between surface water and water supply sources. The similarity can be demonstrated in **Figure 6.5** with linear relation R^2=0.8 and a=1.13 for PFOS and R^2=0.8 and a=0.84 for PFOA. Values a near unity indicates that contamination could not be removed through water treatment steps.

VI.4 SUMMARY

This chapter shows concentration of tap water samples collected from various locations in Yodo River basin (N=15), in other part of Japan (N=30), and other countries (N=37). Conclusions are as follows.

VI.4.1 Conclusion about concentration levels

1) The majority of samples collected were detected with PFOS and PFOA (98% in Japan for both PFOS and PFOA and 77% PFOS and 78% PFOA in other countries). Geomean (range) of concentrations in ng/L in Yodo River (N=15), in the other part of Japan (N=30) and outside Japan (N=37) were 2.65 (0.9-8.4); 0.48 (0.01-9.13); and 0.50 (0.03-13.8) respectively. Corresponding values for PFOA were 11.8 (6.4-42.4); 1.4 (0.03-15.1), and 1.1 (0.05-109.3) in other countries.

2) Concentrations of tap water collected in Yodo River basin were quite less variable and generally higher than those in other part of Japan (geomean of 2.65 ng/L versus 0.48 ng/L and 11.8 ng/L versus 1.4 ng/L). The difference were significant for PFOA (p=0.001, t-test) and quite significant for PFOS (p=0.04)

3) Concentration from different sampling locations in Japan, and different sampling areas in other countries were quite variable. However, concentrations of tap water collected in the same areas often had low-variance, as in most of the cases coefficient of variation was less than one. Concentrations seemed to be high in China and Thailand. Further investigation is needed to confirm the levels of contamination.

VI.4.2 Conclusion about relationship with surface water

4) In general, concentrations levels (geomean of concentrations) of tap water samples collected within an area were in the same levels as those of surface water (a=0.71 , R= 0.47 for PFOS and a=0.91, R= 0.84 for PFOA).

5) Case study in Kinki Region (Japan) and Istanbul (Turkey) demonstrated similar levels of both PFOS and PFOA in tap water to those of water supply sources. The results suggested that PFOS and PFOA, at the levels of several ng/L to several tens ng/L were not effectively removed through water treatment steps.

CHAPTER VII

MASS FLUX ANALYSIS

VII.1 INTRODUCTION

Chapter V indicated that concentrations of both PFOS and PFOA were relatively high in water environment of Yodo River system (Japan) and Singapore. It was also indicated that concentrations in WWTP discharges were distributed in the high range of concentration measured in surface waters. This chapter, water system and spatial distribution of the concentrations in Yodo River and Singapore will be shortly reviewed. Then, the concentrations were used to estimate mass fluxes of PFOS and PFOA in these two sampling areas with focus on WWTPs discharges. This chapter aims at (1) mass discharge and mass behavior of PFOS and PFOA in Yodo River system (2) mass discharge of PFOS and PFOA from WWTP in Singapore, in an attempt to search for the sources of PFOS and PFOA.

VII.2 MATERIALS AND METHODS

VII.2.1 Yodo River system, Japan

Table 7.1 Yodo River basin characterization

Catchment area	8,240 (km^2)
Length of main River	75 (km)
Yearly average discharge	268 (m^3/s)
Population in the basin	11,000,000
Population receive water supply	13,930,000 11,140,000 (Yodo R.)

The Yodo River system runs through the Kinki region of Japan where over 13 millions people lives and is one of the most important River in Japan**.** It has a catchment area of approximately 8,240 km^2. Most wastewater is discharged in the upper river basin, while most drinking water is abstracted downstream. **Table 7.1** shows characterization of Yodo River basin.

Yodo River is the main river in the basin, which receives water from Lake Biwa through Uji River, and water from two other upstream rivers of the Katsura River and the Kizu

River. Three surveys were conducted in the mid and lower basins of Yodo River including Ai River which run in parallel with Yodo River (**Figure 7.1**). Sampling surveys were conducted in three dates: 2004-11-25, 2005-03-16, and 2005-11-1 to collect river water at 34 locations and WWTP discharge at 10 locations. On a sampling date, sampling survey was conducted by several teams so that all samples were together collected within a short period of times (approximately 8 hours).

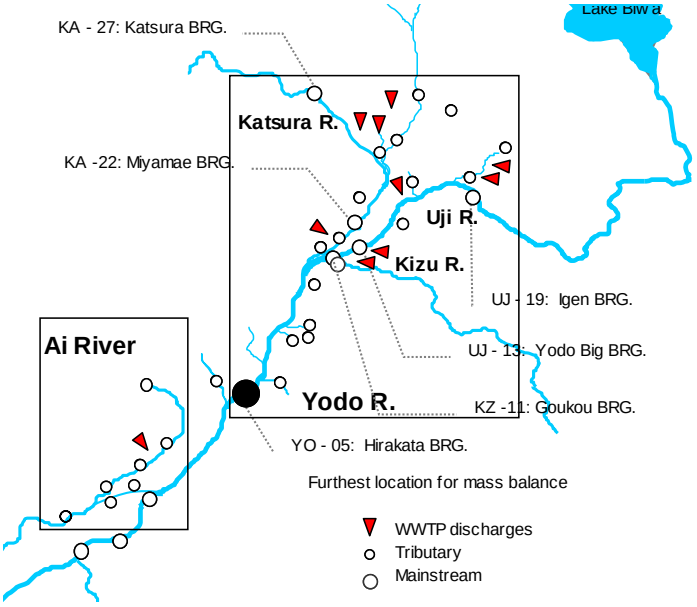

Figure 7.1 Sampling location in Yodo River system and points of mass fluxes analysis

Table 7.2 Investigated WWTP in Yodo River system

	WWTP	Catchment	Treatment Area (ha)	Treatment capacity (m^3/day)	Population
1	BW-W11	Lake Biwa	1,398	9,527	32,331
2	BW-W12	Lake Biwa	13,965	204,450	585,903
3	BW-W13	Lake Biwa	1,387	49,530	98,103
4	BW-W14	Lake Biwa	7,930	78,200	224,187
5	UJ-W04	Uji River	3,502	100,490	299,000
6	UJ-W05	Uji River	2,034	93,697	210,800
7	UJ-W06	Uji River	1,910	86,737	148,700
8	UJ-W08	Uji River	452	14,667	47,264
9	UJ-W09	Uji River	NA	1,000	NA
10	KA-W01	Katsura River	8,137	430,040	771,200
11	KA-W02	Katsura River		103,953	
12	KA-W03	Katsura River	3,801	140,412	324,386
13	KA-W07	Katsura River	587	57,450	81,900
	Total		47,131	1,411,039	2,932,699

Figure 7.1 shows sampling location in Yodo River system and points of consideration for mass fluxes analysis. Mass balance will be analyzed in Yodo River and Ai River. Mass fluxes will be estimated in mainstream, tributary stream as well as in WWTP discharges and mass balance will be analyzed.

Table 7.2 shows characterization of 13 investigated WWTP. Repeated sampling and mass fluxes were estimated for WWTP discharge water to Katsura River catchment (KA-W01, 02, 03, 07) and Uji River catchment (UJ-04,05,06,08,09). The other WWTP discharge (BW-W11,12,13,14) were additionally investigated in Dec-2006 to search for the source of PFOS and PFOA in upstream basin and their locations are not shown in Figure 7.1. Totally, investigated WWTP had an approximately treatment area of 471 km^2 collecting wastewater from approximately 3 million people and discharging water at approximate flow rate of 1,500,000 m^3/d. Information on industrial waste was not available.

VII.2.2 Singapore

Singapore is an island and urban city-state with no rural hinterland. It has the population of about 4 million people in the land area of about 600 km^2. Without natural freshwater rivers and lakes, the primary domestic source of water in Singapore is rainfall, collected in reservoirs or water catchment areas, which account for approximately 50% of Singapore's water. The remainder is mainly imported from Malaysia. Domestic wastewater and industrial wastewater were collected in sewer and treated before discharging to Singapore Straits and Johor Straits. Location and treatment capacity of the WWTPs are shown in **Figure 7.2.**

Figure 7.2 Wastewater treatment plant in Singapore

Table 7.3 WWTP in Singapore

	Treatment capacity	Water body receive discharges	WWTP discharges	Sampling	Discharge rate	Industrial source	Domestic source
SG-W1	232,000	Singapore Straits	W1	●	230,000	5%-10%	90%-95%
SG-W2	282,000	Singapore Straits	W2	●	282,000		
SG-W3	361,000	Singapore Straits	Total		361,000		
			W3 (1)	●	210,000		
			W3 (2)	●	76,000		
			W3 (3)	x	75,000		
SG-W4	205,000	Singapore Straits	W4	●	140,000	60%	40%
SG-W5	151,000	Johor Straits	Total		190,000		
			W5 (1)	●	110,000	60%	40%
			W5 (2)	●	80,000	40%	60%
SG-W6	247,000	Johor Straits	Total		93,910		
			W6(1)	●	50,140		
			W6(2)	●	61,910		
			W6(3)	●	81,860		
Total	1,478,000				1,446,900		

VII.2.3 Mass loading estimation

Flow rates of tributary streams were measured during the sampling, while those of main streams and WWTP discharges were obtained as reported data from Yodogawa River Office (Ministry of Land Infrastructure and Transport) and STP offices respectively.

$$\mathbf{L\ (g/d)\ = C\ (ng/L)\ x\ Q\ (m^3/d)\ x\ 10^6}$$

Where L: estimated daily mass loading (g/d)

C: concentration in the sampling day (ng/L)

Q: collected/ measured daily flow rate (m^3/d)

VII.3 MASS BEHAVIOR IN YODO RIVER SYSTEM

VII.3.1 Concentrations

VII.3.1.1 Distribution of concentrations

Contamination surveys of Yodo River (Chapter V) indicated that PFOS and PFOA concentration fluctuated in a relatively wide range of 0.4-111 ng/L PFOS and 4.2- 43,900 ng/L PFOA in surface water samples and 1.8 - 123 ng/L PFOS and 17 - 8,000 ng/L PFOA in WWTP discharges. It was also indicated that relatively high concentrations of PFOS and PFOA seemed to distribute throughout the basin but highest levels of concentration were often measured in WWTP discharges or tributary streams receiving WWTP discharges, with exceptionally high PFOA concentration repeatedly measured in Ai River catchments. The concentration were also reproducible among sampling dates as discussed in Chapter V. Spatial distribution of PFOS and PFOA concentration could be depicted in **Figure 7.5**.

VII.3.1.2 Stability of concentration along the width of Yodo River

Daily mass loadings were estimated, by the products of grab sample concentrations and daily flow rate data, as shown in the methodology section. Therefore, estimated results are considered to be practical when grab sample concentration fluctuated less in terms of space and times. Reproducibility of concentration might partly reflect the stability of concentration with the time. It is also needed to show consistence of concentrations throughout the width and the depth of the river.

	Concentration (ng/L)	
Sampling location	PFOS	PFOA
YO - 03 North	2.7	32.8
YO - 03 Center	2.3	34.3
YO - 03 South	2.7	33.9
CV	**0.11**	**0.02**
YO - 05 North	2.5	35.0
YO - 05 Center	2.8	28.3
YO - 05 South	2.9	31.2
CV	**0.07**	**0.11**

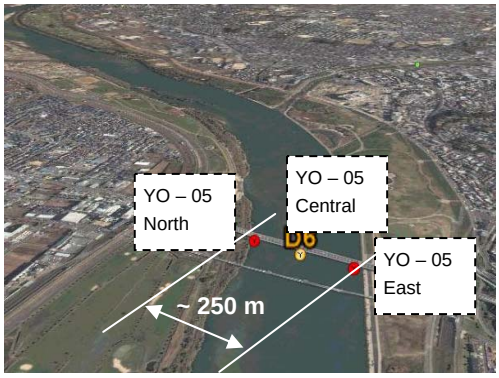

Figure 7.3 Concentrations along width of Yodo River

At two mainstream sites of Yodo river YO - 03 and YO - 05, sampling were conducted in two sides of the river width in addition to the normal centre sampling location. This additional sampling was conducted in 2005-11-1. The width of sampling locations were approximately 250 m for both sampling locations. Concentrations are shown in **Figure 7.3** which indicates significant stability of concentration for both PFOS and PFOA in relatively

low concentrations (several ng/L) for PFOS and relatively high range (several ng/L) for PFOA. For 4 cases, *CV* of concentrations fluctuated around 10% at maximum.

VII.3.2 Flow rate contribution in Yodo River

Figure 7.4 illustrates main flows in Yodo River and average flow rates on three sampling days. The average flow rates in mainstream of the Yodo River were 14,200,000 m^3/day at YO – 03 (Hirakata Bridge), which largely contributed by Uji River. Flows from Katsura River and Kizu River were quite comparable and together account for one thirds of Yodo River flow. Since PFOS and PFOA are not decomposable and sampling were conducted in a short period of time, it was expected that mass loading of all upstream flow are comparable to those of Yodo river downstream.

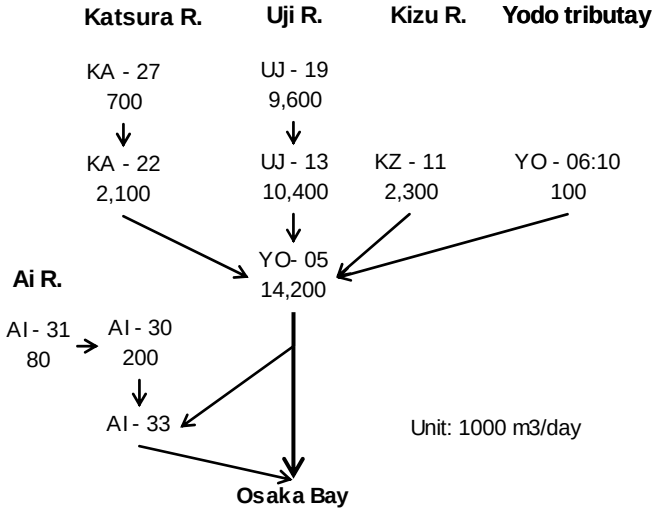

Figure 7.4 Main flows in Yodo River basin and average flow rates of three sampling dates

VII.3.3 Mass fluxes analysis in Yodo River

Mass fluxes were estimated throughout the sampling area at locations of mainstream, tributary and WWTP discharges. An example of mass fluxes behavior together with ranges of concentration on a sampling day (2006-11-03) are illustrated in **Figure 7.5**. **Table 4.6** summaries mass fluxes estimation and contribution in mainstream flows on three sampling days.

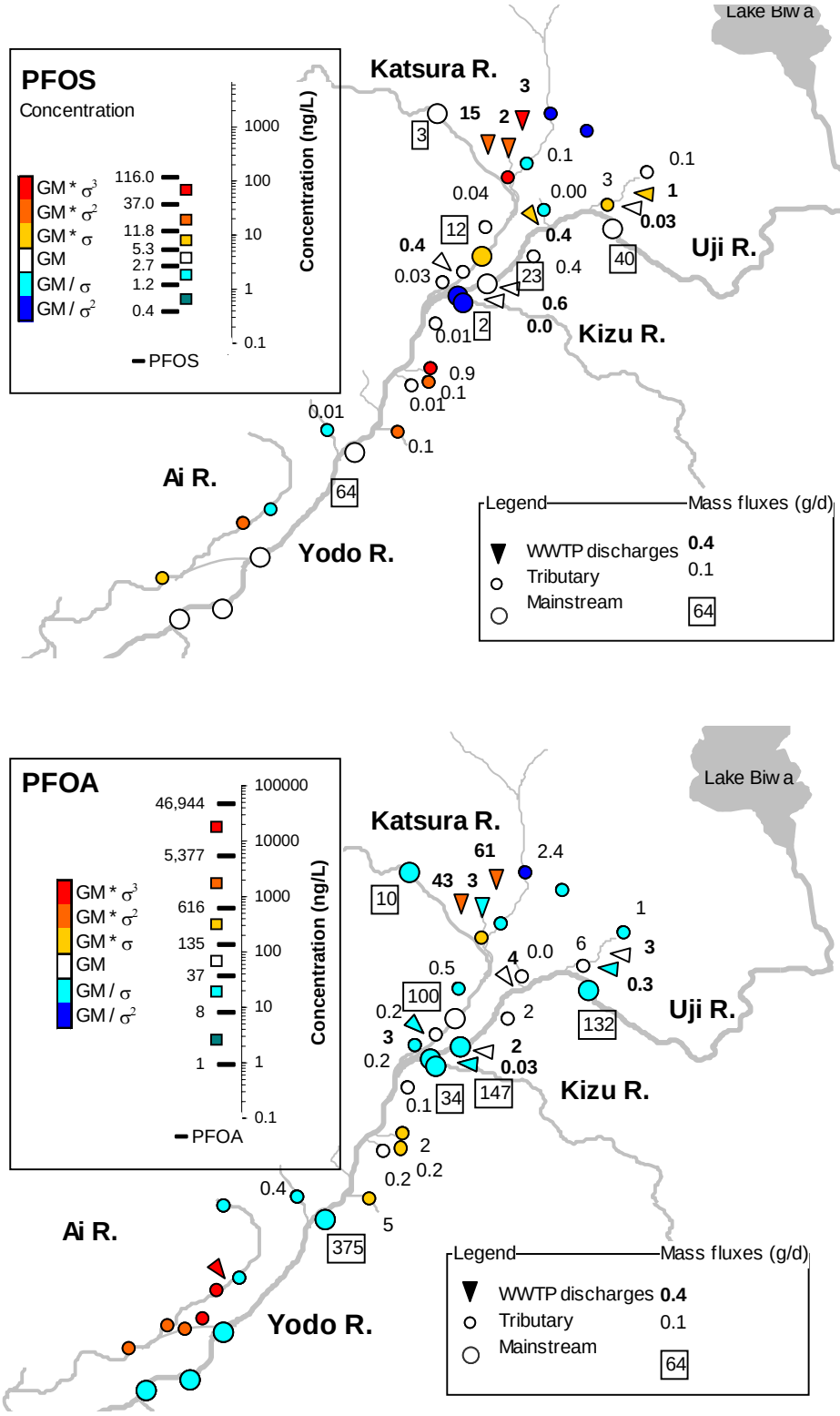

Figure 7.5 Profiles of concentrations and mass behavior in Yodo River in 2005-3-16

Table 7.4 Estimation of PFOS and PFOA daily mass loading in Yodo River basin

Location	Catchment	Location		PFOS mass loading (g/d) Nov-04	Mar-05	Nov-05	PFOA mass loading (g/d) Nov-04	Mar-05	Nov-05
To	Katsura	**KA - 27**		2	3	0	5	10	1
YO - 05		To KA - 22		-	18	23	-	116	1,148
		KA - 22	*	17	11	21	104	100	173
		Down KA - 22	*	-	0	1	-	3	5
	Uji	**UJ - 19**			40	7		132	85
		To UJ - 13		-	45	10	-	144	103
		UJ - 13	*	16	23	17	273	147	177
		Down UJ - 13	*	-	1	1	-	2	13
	Kizu	**KZ -11**	*	3	2	2	41	34	39
	Yodo Downstream	**East Tributaries**	*	-	1	5	-	7	64
To YO - 05 (sum up *)				36	38	47	418	292	470
YO - 05				28	64	27	343	375	272

Mass flux at mainstream location YO -05 (Hirakata Bridge) was estimated as 28 g/d, 64 g/d, 29 g/d for PFOS and 343 g/d, 375 g/d, 271 g/d for PFOA on sampling day 1, day 2 and day 3 respectively. Mass fluxes seemed to be stable among sampling dates. With assumption of reproducible concentration all year around, discharge rate of PFOS and PFOA in Yodo River could be estimated by

Yearly discharge (kg/year) = Average daily mass flux (g/day) * 365 (day/year) /1000.

Therefore, estimated amount of 15 kg/year PFOS and 120 kg/year PFOA are expected to discharge from Yodo River (Hirakata Bridge) to Osaka Bay

VII.3.3.1 Pathways of PFOS and PFOA to Yodo River

In order to search for pathways of PFOS and PFOA in Yodo River (Hirakata Bridge YO-05), firstly it is needed to confirm mass balance from upstream flows to downstream flows YO-05. **Figure 7.5** shows PFOS and PFOA mass loading contribution from upstream rivers and tributaries to downstream site YO - 03. Flow rates and chloride are also shown in the figure for mass balance check. Total cumulative loads of upstream were close to value 100% of downstream YO - 03. Even though fluctuations could be seen there is observation that fluctuation were at same level for different parameters of flow rate, chloride, PFOS and PFOA in individual sampling date with. The biggest different is

observed in the third sampling day. Similarities in total upstream loads to those of downstream reflect the lack of either sink or rise of PFOS and PFOA during transportation.

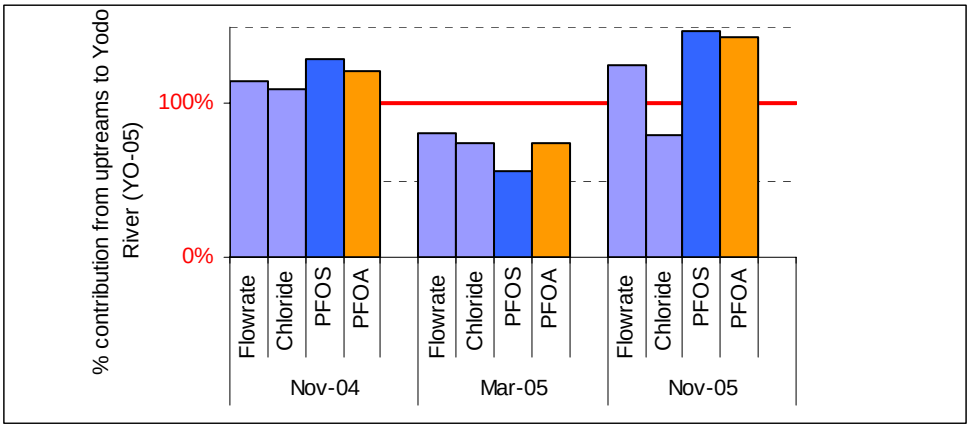

Figure 7.6 Mass balance check

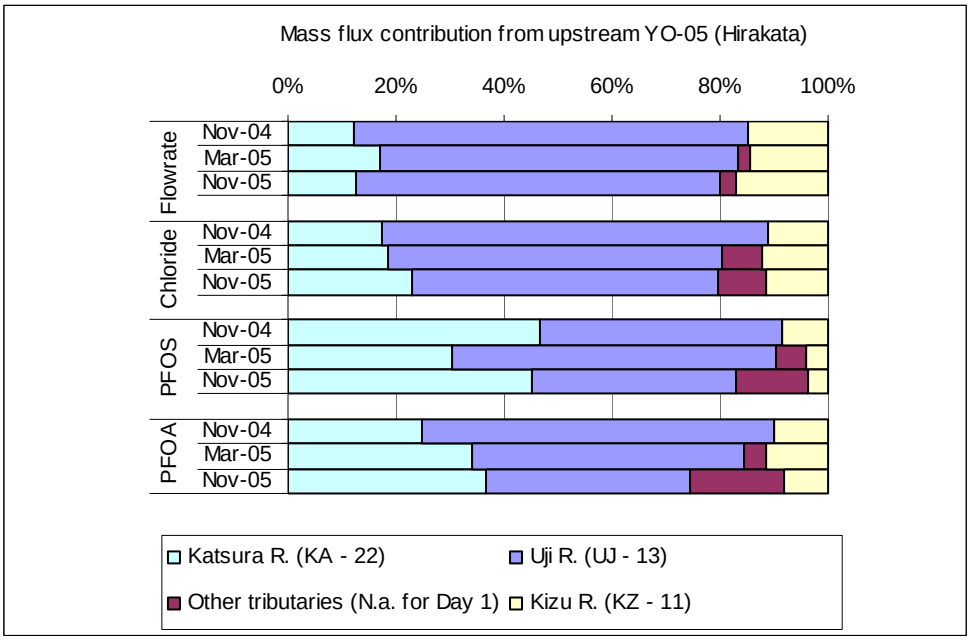

Figure 7.7 Mass loading contribution from upstream of Yodo River YO-05

Figure 7.7 shows mass flux contribution pattern from three upstream rivers and other tributaries to YO-05 in terms of PFOS and PFOA, flow rate and chloride. Contribution patterns of flow rate and chloride were similar but they were different from those of PFOS as well PFOA. Katsura River often had higher fractions of PFOS and PFOA loads than its flow rate. Main finding was that PFOS and PFOA contaminations were largely contributed

by Uji River (about 50% in average) and Katsura River (about 40% in average). Therefore main pathways of PFOS and PFOA in Yodo River must be through Uji River and Katsura River

VII.3.3.2 Contribution from WWTP discharges to Katsura R. and Uji R.

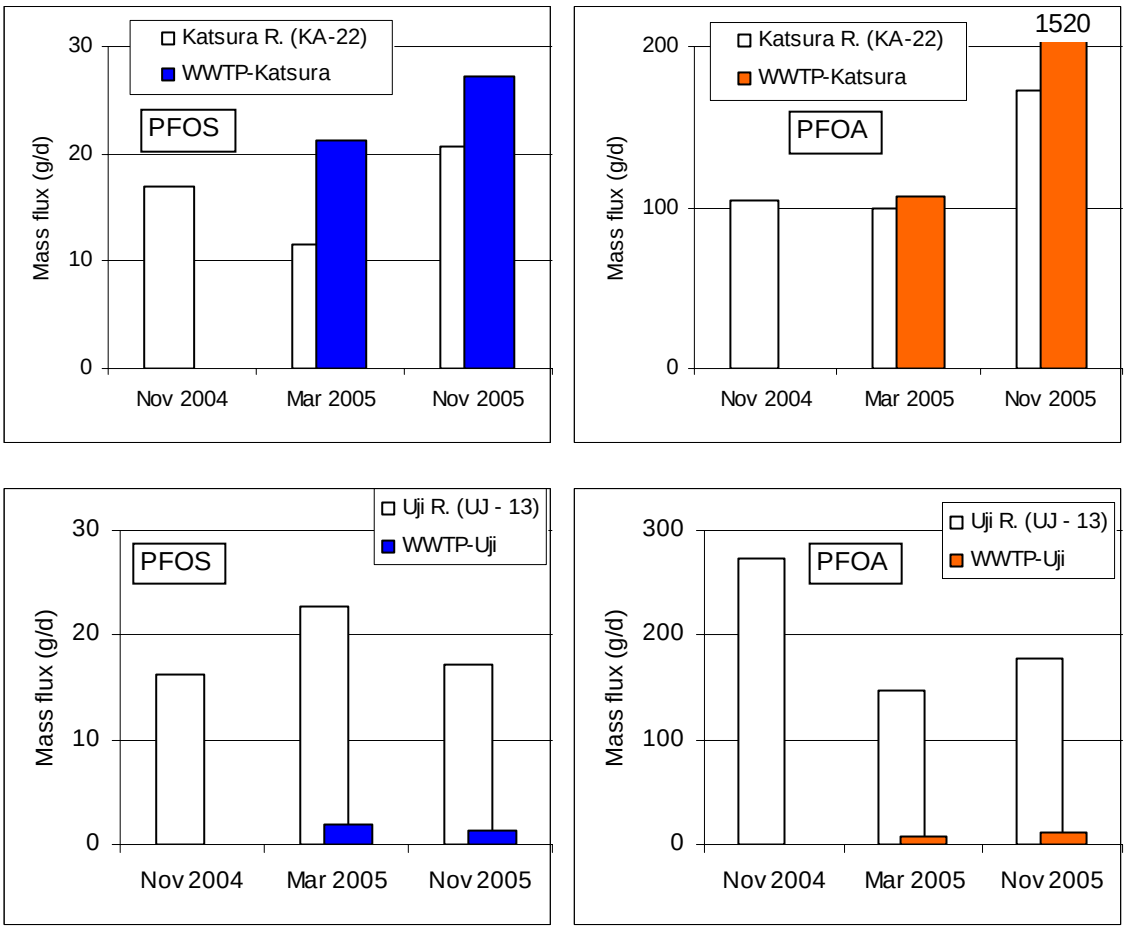

Figure 7.8 Mass fluxes in Katsura River and Uji River and contribution from WWTP discharges

There is need to search for source PFOS and PFOA in Katsura River and Uji River. In Katsura River, elevated mass loading was also observed from upstream sampling locations KA - 27 to downstream sampling location KA - 22 (**Table 7.4).** Increases were observed for both PFOS and PFOA and the observation were repeatedly found in three sampling dates with several times to hundred times higher mass loading. Specifically, PFOS, mass increased from 2 to 17 g/d, from 3 to 11 g/d, from 0 to 21 g/d in three sampling dates while those of PFOA increased from 5 to 104 g/d, from 10 to 100 g/d, and from 1 to 173 g/d

respectively. Quite consistently with this elevation, total mass from upstream of KA - 22 were comparable with those in KA - 22 with exception of even higher load of PFOA in sampling day 3 as illustrated in **Figure 7.8**. These mass loads were largely contributed by three WWTPs discharges KA - W01, KA - W02, and KA - W07 which either flow to Nishi Takase River and finally to Katsura River or directly flow to Katsura River. It is calculated that loads of these three effluents occupied at least 89% for PFOS and 88% for PFOA of total loads from all flows going to KA - 22. Therefore, those WWTPs discharges must be main sources of contamination in Katsura River.

In Uji River, contamination loads in the upstream sampling site were relatively high (about the levels of the downstream site loads) as shown in **Table 7.5**. On the other hand, mass flux contribution from WWTP discharge account for very small fraction of downstream flux as depicted in **Figure 7.8**. It is supported that that pollution of PFOS and PFOA must be from upstream basin - Lake Biwa basin.

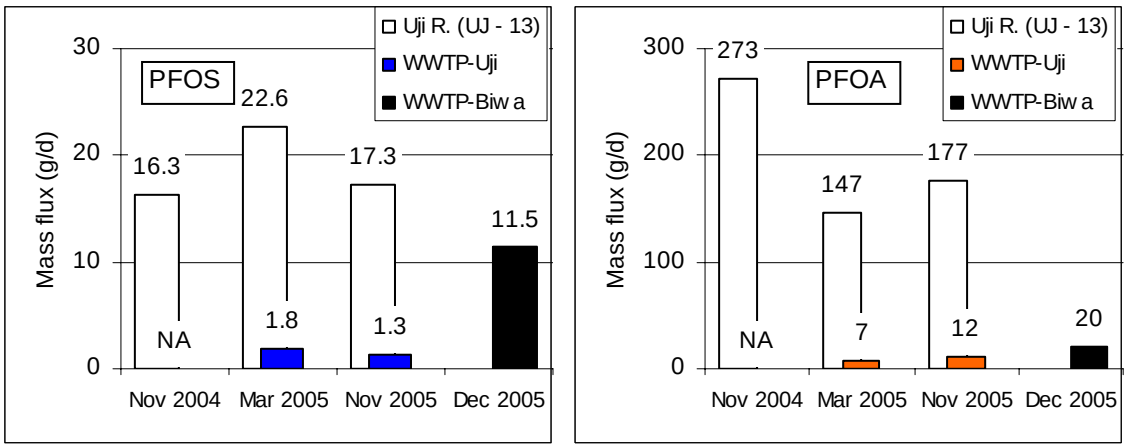

Figure 7.9 Comparison of mass fluxes from WWTP in Lake Biwa basin and Uji River

Therefore, additional investigation of WWTP discharges from Lake Biwa basin were conducted as mention in methodology (UJ-BW11, 12, 13, 14). As a result, an estimation of 11.5 g/d PFOS and 20 g/d PFOA were discharged from WWTP in Lake Biwa basin. In terms of PFOS, mass flux from WWTP in Lake Biwa can be accounted for significant portion of those in Uji River (11.5 g/d from WWTP-Biwa versus 18 g/d (average) in Uji River as depicted in **Figure 7.9**. In combination with WWTP in Uji River catchment, WWTP discharge could account for an approximate value of 70% mass flux in Uji River.

Differently, mass flux of PFOA from WWTP-Biwa were less significantly contributed to those of Uji River as depicted in Figure 7.9. Totally, an estimation 15% of PFOA in Uji River was contributed by investigated WWTP in Uji River catchment and Lake Biwa catchment.

VII.3.3.3 Behavior of PFOS and PFOA among WWTP discharges

It is important to know the original sources of the chemicals transported through WWTPs. Exceptional high concentration levels of PFOA in WWTP discharge AI - W10 in Ai River seems to not only related with population but a factory located near the WWTP. In this section, nine WWTPs discharges in Katsura R. catchment and Uji R. catchment is further analyzed. These WWTPs contained domestic wastewater of nearly 2 millions residents as mentioned above. In fact, PFOS and PFOA from a WWTPs discharges could originate from various sources such as domestic wastewater (possibly from cleaning and care of surface-treated products), industrial wastewater, runoff, etc.

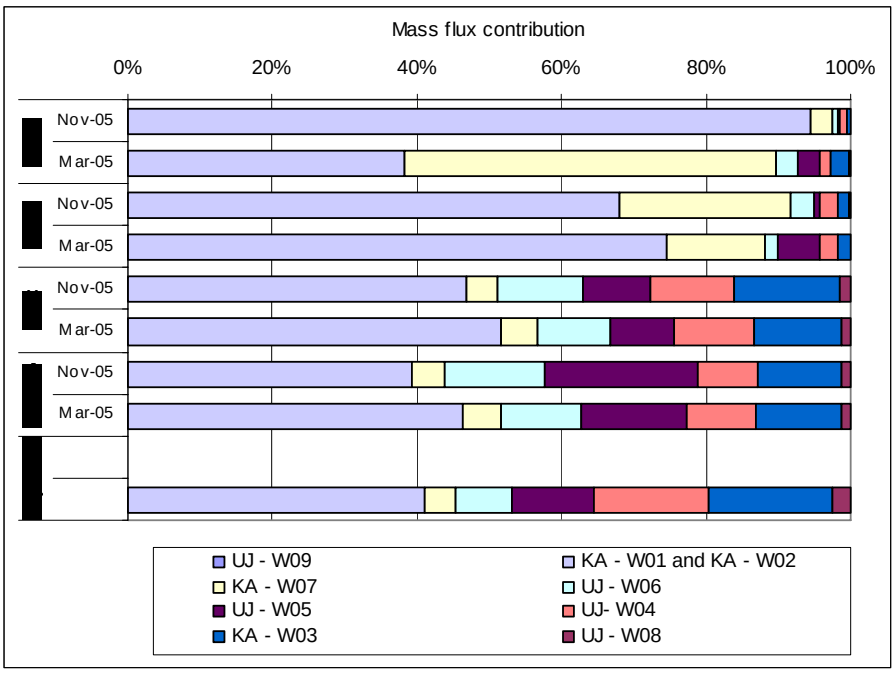

Figure 7.10 Contribution pattern among WWTPs discharges in terms of population, chloride, DOC, PFOS and PFOA

It is examined the relation of PFOS and PFOA contaminants with domestic-wastewater related items in terms of load. **Figure 7.10** shows contribution patterns of population

served by WWTPs, chloride, DOC, PFOS and PFOA from each WWTP to those of all WWTPs. The contribution patterns of both PFOS and PFOA loads were quite different from those of population, chloride, and DOC, which were similar. Particularly, KA-W01, KA-W02 and KA-W07 totally contributed less than 60% in terms of population, chloride, and DOC while often accounted for more than 90 % in terms of PFOS and PFOA. It is likely that significant sources of PFOS and PFOA in highly contaminated WWTPs discharges were from non-domestic wastewaters going to those WWTPs.

VII.3.4 Mass flux in Ai River

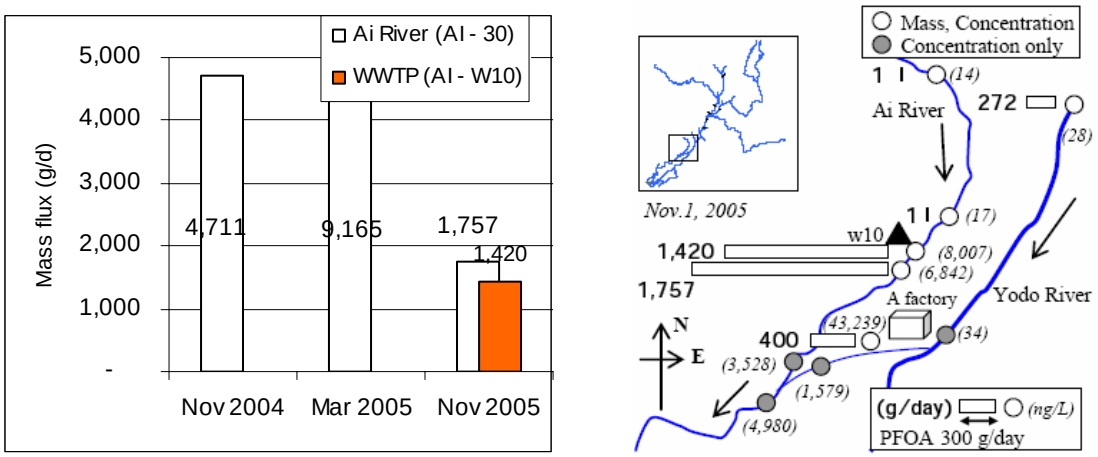

Figure 7.11 Mass fluxes Ai River AI-30 in three sampling date and contribution of WWTP discharge AI-W10

In Ai River, while mass loading were quite neglectable for PFOS (several g/d), relatively high mass loading was calculated for PFOA at 4,711 g/d, 9,615 g/d, and 1757 g/d respectively which was approximately tens times higher than those in Yodo River. A possible yearly discharge of 2 tons of PFOA could be expected.

Figure 7.11 shows mass estimation in Ai River at sampling site (AI-30), 100 m downstream of WWTP discharge AI-W10. Mass fluctuated at several thousand g/d which were several times compared to concentration and mass fluxes estimation of PFOA in Ai River. While PFOA concentration increased significantly after discharge point of WWTP AI-W10. Available data on day 3 showed elevated concentration and mass loading was observed from upstream sites sampling location AI - 31 to downstream sampling location AI - 30, with an approximately mass loading of 1g/d upstream and thousand times increase downstream at 1,757 g/d. The AI -31 is just 200m upstream from WWTP AI-W10 while

AI-31 is 100 m downstream of this WWTP discharge. At the same time, a comparable load of 1,420 g/d were estimated in the effluents (Table 4.5). It can be concluded that the WWTP is suggested a main source of PFOA in Ai River.

VII.4 MASS FLUX FROM WWTP DISCHARGES IN SINGAPORE

VII.4.1.1 Concentration distribution

PFOS and PFOA concentration fluctuated largely within each type of water: reservoir water, non-catchment streams and WWTP discharges. However, maximum concentration in WWTP were ten times higher than that in other groups for PFOS and several time for FPOA. Those concentration were several hundred ng/L.

VII.4.1.2 Mass flux from WWTPs discharges

Table 7.5 Flow rate data and estimation of mass fluxes in WWTPs discharges in Singapore

WWTP discharge	Q (m^3/d)	Sampling	PFOS (g/d)	PFOA (g/d)
SG - W1	230,000	●	107.41	29.37
SG - W2	282,000	●	3.92	3.54
SG - W3 (1)	210,000	●	1.55	2.67
SG - W3 (2)	76,000	●	0.80	1.06
SG - W3 (3)	75,000	NA	NA	NA
SG - W4	140,000	●	29.53	11.92
SG - W5 (1)	110,000	●	4.05	47.57
SG - W5 (2)	80,000	●	0.37	2.80
SG - W6(1)	50,140	●	1.79	5.96
SG - W6(2)	61,910	●	2.00	3.21
SG - W6(3)	81,860	●	0.57	0.78
Total	1,396,910		152	109

Note: NA indicates "not available"

Mass flux calculation was based on analyzed results of concentration and collected flow rates. **Table 7.5** shows estimation results. Total day amount of 152 g/d PFOS and 109 g/d PFOA would be higher and comparable to those from Yodo River basin. With assumption that concentration and flowrate is daily and yearly representative, yearly discharging

amount from WWTP discharges in Singapore would be 152 (gPFOS/d) * 365 (d/yr) which is equal to 55 kg PFOS and 109 (gPFOA/d) * 365 (d/yr) which equal to 39 kg/year PFOA.

Table 7.5 shows that mass fluxes contribution of either PFOS or PFOA was mainly contributed by several WWTP discharges. **Figure 7.12** indicated that two WWTP discharges SG-W4 and SG-W5(1) could contribute to a large portion of total mass discharge from all WWTP while contributing about 20% portion of total flow discharges. These two WWTP discharges, therefore, considered to be significant sources of PFOS and PFOA. The figure indicated that PFOS and PFOA might not be only related with flowrate (or domestic activity) alone. This is supported by the fact that approximately 60% of wastewater sources of this two effluent was contributed by industrial sources as shown in Table 7.3.

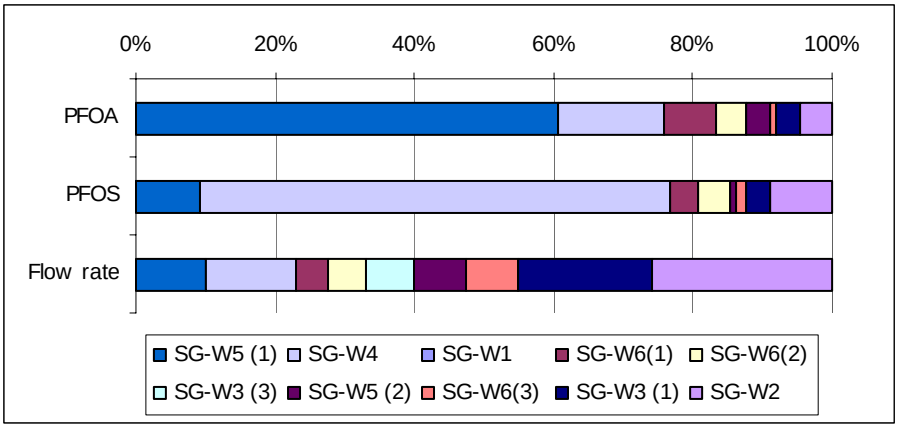

Figure 7.12 Mass fluxes contribution by WWTP discharges in Singapore

VII.5 SUMMARY

Previous chapter indicated that concentration levels of both PFOS and PFOA were high in Yodo River and in Singapore. Using the measured concentration and flowrate data, mass fluxes were estimated in an attempt to search for main sources of contamination.

VII.5.1 Mass behavior in Yodo River system

1) Mass flux was estimated indicating a possible yearly discharge of 15 kg PFOS and 120 kg PFOA in Yodo River to Osaka Bay.

2) In Yodo River, mass flux analysis suggests that important pathway of both PFOS and PFOA to downstream water is through Uji River (50%) and Katsura River (40%). Contamination in Katsura River were mainly contributed by three WWTP discharges in Kyoto City while main contamination contribution of Uji River must be due to upstream Lake Biwa basin. Further investigation of WWTP discharges from Lake Biwa suggested a contribution of approximately 70% PFOS by investigated WWTP discharges from Lake Biwa and Uji, but 15% for those of PFOA.

Therefore, the results pinpoint the important direct sources of PFOS (at least 70%) and PFOA (at least 40%) by several WWTPs which had catchment area and population of about 5% and 30% of those in the whole basin.

3) Among investigated WWTPs discharges to Uji River catchment and Katsura River catchment, analysis of PFOS and PFOA with population and DOC and chloride indicated different patterns of both PFOS and PFOA to domestic water quality items. High contribution of PFOS and PFOA is not always related with high contribution of population and flow rate, or DOC and chloride, which were similar to each other. On the other hand, there was little relation of PFOS and PFOA concentration with both DOC and chloride throughout the basin, as shown in **Chapter V.** This two spices of results suggested that major sources of PFOS and PFOA was not only due to domestic activity.

4) In Ai River where high concentration level of PFOA often observed, it is estimated a possible yearly discharge of several tons of PFOA from Ai River to Osaka Bay. PFOA contamination was largely due to a WWTP discharge.

VII.5.2 WWTP discharges in Singapore

5) Estimation of mass fluxes in Singapore indicated that WWTP discharges could produce a possible yearly mass flux of 55 kg PFOS and 39 kg PFOA. These amounts are four times higher than those of Yodo River for PFOS (15 kg/year), but three times lower than those of Yodo River for PFOA (120 kg/d).

6) Major portion of these sources were contributed by only two WWTP discharges where 60% of industrial wastewater contributed.

CHAPTER VIII

CONCLUSION AND RECOMMENDATIONS

VIII.1 CONCLUSIONS

PFOS and PFOA are man-made chemicals which are persistent and widely distributed in living organism. Due to their persistent characteristic and potential toxicity, study PFOS and PFOA in environment is of important. The environmental compartment of concern is water but their concentration levels as well as behavior in water environment are not well understood. Specially, concentration data is far less enough for understanding behavior of PFOS and PFOA in a local scale as well as in global scale.

The research aims to study pollution of PFOS and PFOA in water environment, with focus their distribution and behavior in surface water, wastewater treatment plant (WWTP) discharges and tap water. Analysis method was developed and sampling campaigns were conducted to collected water samples from various locations for analysis of PFOS and PFOA. Water pollution of PFOS and PFOA were examined in three parts. Firstly, distribution of concentrations from various environmental waters was studied. Then, concentrations of tap waters were investigated and affect from environmental water contamination was examined. Finally, mass flux analysis was conducted to search for source of contaminants in places where high concentration were measured. Main results were as follows.

VIII.1.1 PFOS and PFOA pollution in environmental water (Chapter V)

In order to achieve the second and thrid dissertation objectives, which are to (1) investigate distribution of concentrations of PFOS and PFOA in surface water and to (2) examine concentration of PFOS and PFOA in WWTP discharges, water sampling surveys were conducted in various areas.

Surface water samplings were conducted in Kinki (Japan) (N=15), Shenzhen (China) (N=9), Hanoi (Vietnam) (N=12), Phong River (Thailand) (N=29), Chao Phraya River (Thailand) (N=15), Kota Kinabalu (Malaysia) (N=21), Johor Bahru (Malaysia) (N=6), Singapore

(*N*=24), Orebro (Sweden) (*N*=12), and Turkey (*N*=5) (*N* indicates number of sampling locations). Samplings of WWTP discharges water were conducted in Shenzhen (China) (*N*=1), Singapore (*N*=10), Orebro (Sweden) (*N*=2) and Turkey (*N*=1) together with Yodo River (Japan) (*N*=10) as shown in the previous chapter, (*N* indicates number of sampling locations). In combination with results of Yodo River shown, conclusions were as follows.

Concentrations in surface water

1) Overall 90% and 85% of sampling locations (*N*=185) had surface water concentration above detection limits for PFOS and PFOA respectively. Average concentrations at individual sampling locations varied from <0.05 ng/L to 67 ng/L for PFOS and < 0.1ng/L to 21,600 ng/L PFOA. Median of concentrations in individual survey areas ranged from 0.08 ng/L in Hanoi to 7.1 ng/L in Johor Barhu for PFOS and from 0.1 ng/L in Orebro to 34.4 ng/L in Yodo River for PFOA. This reflects ubiquitous pollution of PFOS and PFOA in surface water environment at ng/L order of concentration.

2) Medians (ranges) of PFOS concentrations in individual areas are ranked as follows: Johor Barhu: 7.3 (0.9-26.1), Singapore: 4.7 (0.4-26.5), Yodo River: 3.4 (0.6-67.4), Shenzhen: 2.5 (1.4-5.2), Kinki 1.4 (0.3-13.2), Chao Phraya River: 1.5 (0.2-2.2), Turkey: 1.0 (0.08-2.15), Orebro: 0.93 (0.5-26), Phong River: 0.16 (ND-0.61), Kota Kinabalu: 0.12 (ND-27.8), Hanoi: 0.08 (ND-1.3). Medians (ranges) of PFOA concentrations are ranked as follows: Yodo River: 34.4 (6.6 - 21,600); Singapore 16.4 (0.7-184); Shenzhen: 14.3 (6.1-109.2); Johor Bahru: 12.9 (5.10-18.9); Kinki: 3.3 (0.4-30.0); Chao Phraya River: 4.2 (1.1-20.4); Turkey: 3.1 (2.8-8.1); Hanoi: 0.91 (ND-6.6); Phong River: 0.66 (ND-4.5); Kota Kinabalu: 0.19 (ND-3.22); Orebro: 0.1 (ND-5.53).

3) Repeated samplings were conducted in Yodo River, Phong River and Kota Kinabalu. Concentrations were significantly reproducible among different sampling dates especially in Yodo River where relatively high concentrations of both PFOS and PFOA were observed (CV of less than 0.3 and 0.5 for 50% and 85 % of sampling locations for PFOA and 40% and 70% for PFOS respectively). The results confirm low contamination levels in Phong River and Kota Kinabalu and high concentration levels in Yodo River.

4) High concentration levels were often found in surface water of urbanized and industrialized areas such as Yodo River, Shenzhen, Johor Barhu, Singapore with median concentrations higher than 2 ng/L for PFOS and 10 ng/L for PFOA. Differences in concentration levels were observed among survey areas within a country, as demonstrated

by the cases of Yodo River and other rivers of Kinki in Japan, Chao Phraya River and Phong River in Thailand, and Johor Bahru and Kota Kinabalu. High concentration levels found in this study were comparable with reported values in the USA while low concentration levels were higher than concentration reported in oceanic water suggesting affect of human activities.

Concentrations in WWTP discharges

5) PFOS and PFOA were detected in all WWTP discharge samples with an exception of a sample in Istanbul. Maximum concentration was measured at several hundred ng/L PFOS and thousand ng/L for PFOA in Yodo River and Singapore. The medians (ranges) of concentrations (ng/L) in Yodo River (N=10) were 8.5 (2.5 - 76.4) for PFOS and 47.8 (32.3 - 8,000) for PFOA. Those in Singapore were 23.1 (4.6 - 467) for PFOS and 43.4 (9.57 - 432.5) for PFOA. Several WWTP samples collected in Shenzhen, Orebro, Istanbul have concentration several to several ng/L.

6) Within a survey area, concentrations in WWTP discharges were often higher than those in surface water. It is suggested that WWTP discharges might be sources of PFOS and PFOA in many areas.

Correlation among different parameters

7) PFOS concentration was typically lower than PFOA concentration. Ratio of PFOS concentration to PFOA concentration (PFOS/PFOA ratio) fluctuated in the range of 0.01-1 (observed for 85% sampling locations) suggesting PFOS and PFOA often co-existed. This is supported by log-linear increasing trend of geometric mean of PFOA concentration versus that of PFOA (R= 0.85).

8) In Yodo River, ratio of PFOS/PFOA ratio fluctuated around 0.1 in Yodo River but when down to 0.001 repeatedly in Ai River, where surface water concentration of PFOA were repeatedly measured at several μg/L, indicating a separated point source of PFOA.

9) In Yodo River, profiles of both PFOS and PFOA were different from those chloride and DOC indicating that there could be little relation between contamination of PFOS and PFOA in the basin with population and nature.

VIII.1.2 PFOS and PFOA contamination in drinking water (Chapter VI)

In order to achieve dissertation objective number four and five, that are to examine contamination of PFOS and PFOA in tap water and their relationship in surface water, sampling of tap water were conducted in Yodo River basin, Japan (N =15), in various locations in Japan (N = 30), and other countries (N = 37). Tap water samples were collected with priority in areas where surface water surveys were conducted. In Kinki region of Japan, where Yodo River is located, survey of tap water and water supply sources were conducted. Main conclusions were as follows.

Concentrations in tap water

1) The majority of samples collected were detected with PFOS and PFOA (98% in Japan for both PFOS and PFOA and 77% PFOS and 78% PFOA in other countries). Geomean (range) of concentrations in ng/L in Yodo River (*N*=15), in the other part of Japan (*N*=30) and outside Japan (*N*=37) were 2.65 (0.9-8.4); 0.48 (0.01-9.13); and 0.50 (0.03-13.8) respectively. Corresponding values for PFOA were 11.8 (6.4-42.4); 1.4 (0.03-15.1), and 1.1 (0.05-109.3) in other countries.

2) Concentrations of tap water collected in Yodo River basin were quite less variable and generally higher than those in other part of Japan (geomean of 2.65 ng/L versus 0.48 ng/L and 11.8 ng/L versus 1.4 ng/L). The difference were significant for PFOA (p=0.001, t-test) and quite significant for PFOS (p=0.04)

3) Concentration from different sampling locations in Japan, and different sampling areas in other countries were quite variable. However, concentrations of tap water collected in the same areas often had low-variance, as in most of the cases coefficient of variation was less than one. Concentrations seemed to be high in China and Thailand. Further investigation is needed to confirm the levels of contamination.

Relationships to surface water

4) In general, concentrations levels (geomean of concentrations) of tap water samples collected within an area were in the same levels as those of surface water (a=0.71 , R= 0.47 for PFOS and a=0.91, R= 0.84 for PFOA).

5) Case study in Kinki Region (Japan) and Istanbul (Turkey) demonstrated similar levels of both PFOS and PFOA in tap water to those of water supply sources. The results suggested that PFOS and PFOA, at the levels of several ng/L to several tens ng/L were not effectively removed through water treatment steps.

VIII.1.3 Mass flux analysis of PFOS and PFOA (Chapter VII)

In order to achieve dissertation objective number six, two areas where high concentrations of PFOS and PFOA in water environmental was observed were selected for mass flux analysis. They are Yodo River system and Singapore. Mass flux was estimated based on measured concentrations and flow rate data and was analyzed with attempt to search for the predominant sources of PFOS and PFOA

Mass behavior in Yodo River system

1) Mass flux was estimated indicating a possible yearly discharge of 15 kg PFOS and 120 kg PFOA in Yodo River to Osaka Bay.

2) In Yodo River, mass flux analysis suggests that important pathway of both PFOS and PFOA to downstream water is through Uji River (50%) and Katsura River (40%). Contamination in Katsura River were mainly contributed by three WWTP discharges in Kyoto City while main contamination contribution of Uji River must be due to upstream Lake Biwa basin. Further investigation of WWTP discharges from Lake Biwa suggested a contribution of approximately 70% PFOS by investigated WWTP discharges from Lake Biwa and Uji, but 15% for those of PFOA.

Therefore, the results pinpoint the important direct sources of PFOS (at least 70%) and PFOA (at least 40%) by several WWTPs which had catchment area and population of about 5% and 30% of those in the whole basin.

3) Among investigated WWTPs discharges to Uji River catchment and Katsura River catchment, analysis of PFOS and PFOA with population and DOC and chloride indicated different patterns of both PFOS and PFOA to domestic water quality items. High contribution of PFOS and PFOA is not always related with high contribution of population and flow rate, or DOC and chloride, which were similar to each other. On the other hand, there was little relation of PFOS and PFOA concentration with both DOC and chloride throughout the basin, as shown in **Chapter V.** This two spices of results suggested that major sources of PFOS and PFOA was not only due to domestic activity.

4) In Ai River where high concentration level of PFOA often observed, it is estimated a possible yearly discharge of several tons of PFOA from Ai River to Osaka Bay. PFOA contamination was largely due to a WWTP discharge.

Mass discharge from WWTPs in Singapore

5) Estimation of mass fluxes in Singapore indicated that WWTP discharges could produce a possible yearly mass flux of 55 kg PFOS and 39 kg PFOA. These amounts are four times higher than those of Yodo River for PFOS (15 kg/year), but three times lower than those of Yodo River for PFOA (120 kg/d).

6) Major portion of these sources were contributed by only two WWTP discharges where 60% of industrial wastewater contributed.

VIII.2 RECOMMENDATIONS

The study results indicated international contamination of PFOS and PFOA in inland surface water from various locations. It is suggested further study on fate and sources of PFOS and PFOA in slightly contaminated areas. For examples, monitoring PFOS and PFOA related compounds as well as possible precursor compounds is recommended.

The study results show contamination of PFOS and PFOA in tap water samples collected from various locations at ng/L level. However, there is little information on safety levels and toxicity of these compounds in drinking water. Further toxicity study is recommended in order to set up international and qualified drinking water standards for PFOS and PFOA. Thus, contamination levels found in this study would be further scientifically evaluated.

The study indicated wastewater treatment plants often discharged water with high concentrations of PFOS and PFOA into environment. Specifically, in Yodo River it was pointed out that several WWTP discharges were significant point sources of these chemicals. Therefore, as a counter measure, removal of PFOS and PFOA from highly contaminated point sources might be needed. Study on removal technology of PFOS and PFOA from water at the levels indicated in this dissertation become necessary in order to control contamination of PFOS and PFOA in water environment in such area.

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